

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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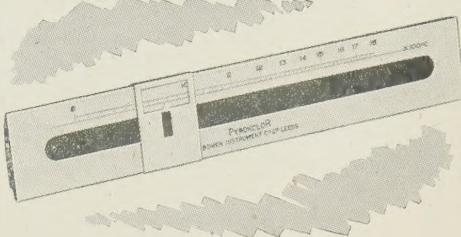
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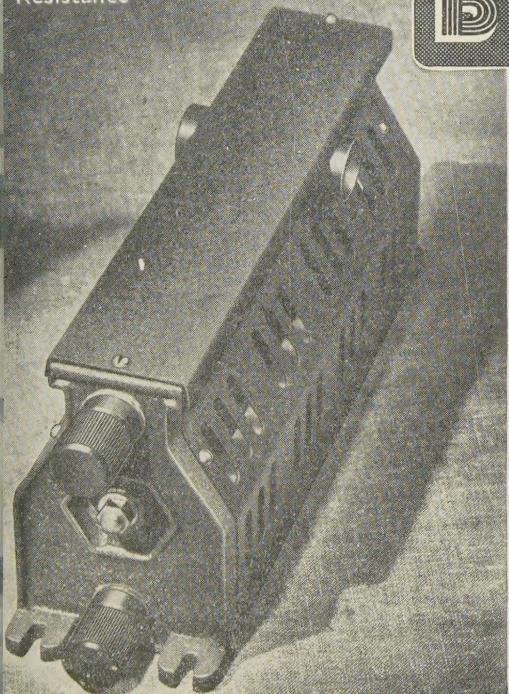


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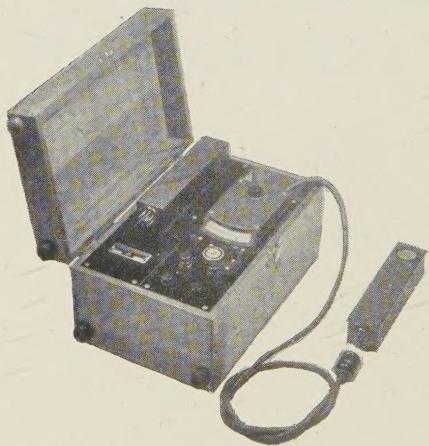
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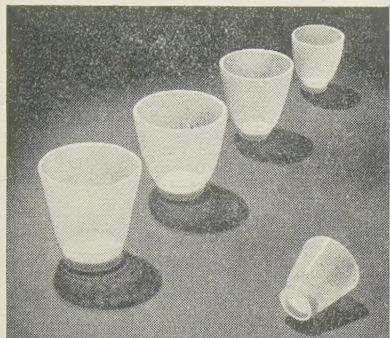
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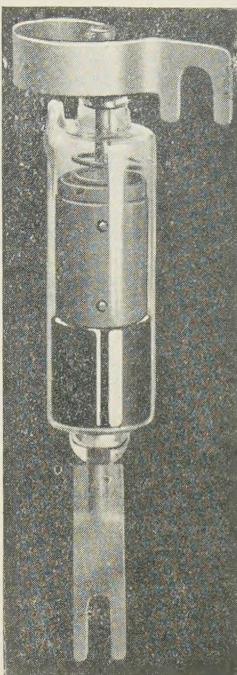
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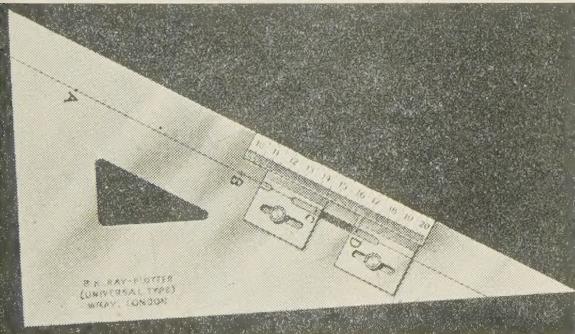
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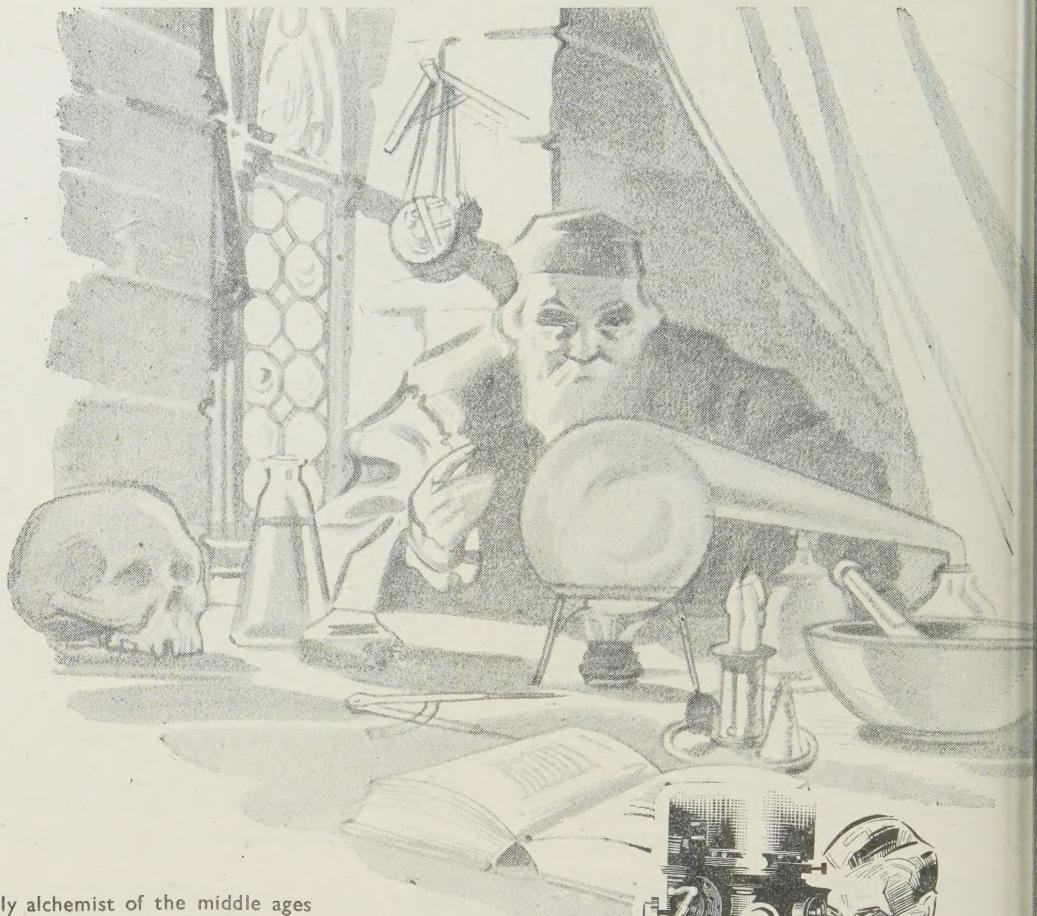


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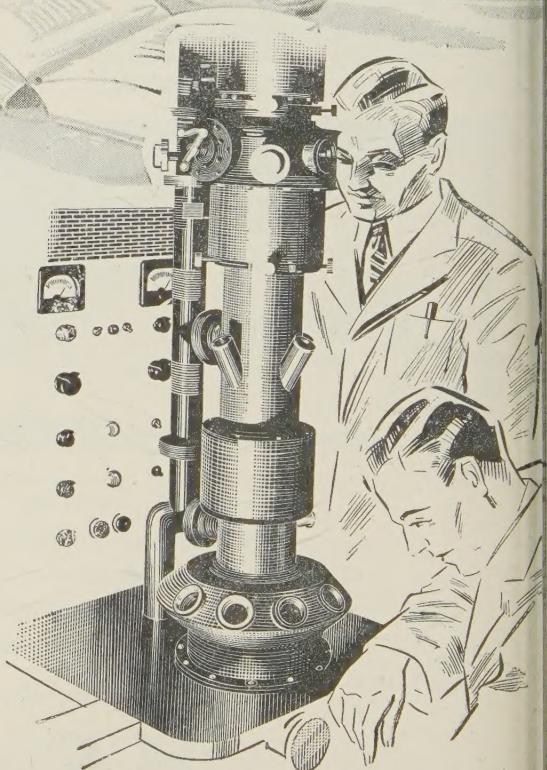
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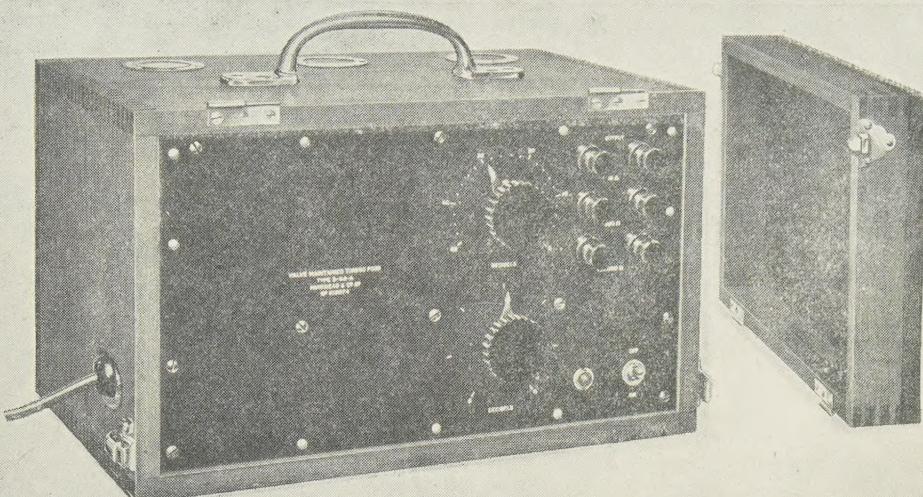
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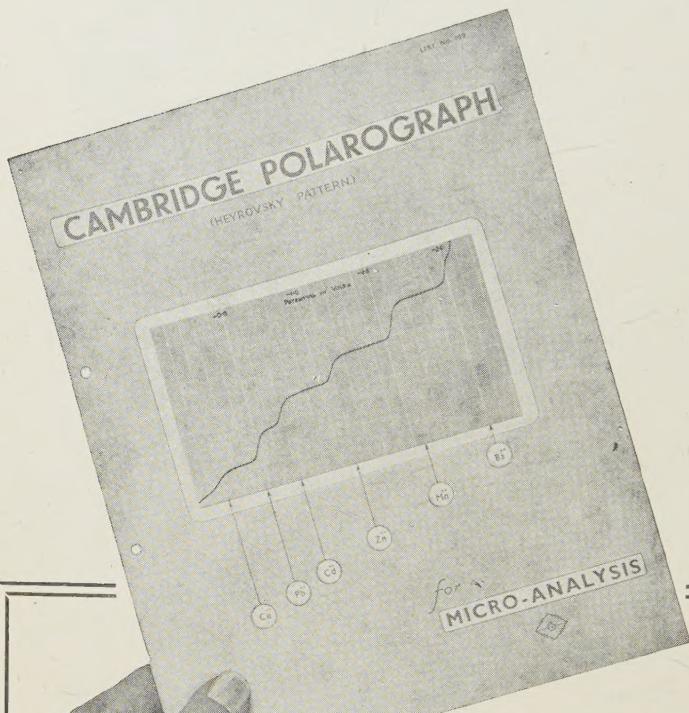
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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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THE THEORY OF INDENTATION AND HARDNESS TESTS

BY R. F. BISHOP, R. HILL
AND
N. F. MOTT, F.R.S.

Received 2 January 1945; read 9 March 1945

ABSTRACT. A discussion is given of the indentation of ductile materials by cylindrical punches with conical heads. On the experimental side, experiments have been made with work-hardened and with annealed copper, with penetrations up to nine times the diameter of the punch. It is found that the load rises towards a maximum value which is not approached until the base of the cone has travelled four to five diameters into the copper block. Denoting this maximum load by p_0A , where A is the area of the cross-section of the punch, it is found that p_0 for a lubricated punch is about twice the hardness, or five times the yield stress, of the work-hardened material. A theoretical method is given for calculating p_0 , as follows: the pressures p_c and p_s required to enlarge a cylindrical and a spherical hole in a material showing any kind of strain hardening can be calculated. It is plausible to assume that p_0 should be between p_c and p_s , and since p_s is only slightly greater than p_c , an approximate theoretical estimate of p_0 is obtained. This is in good agreement with experiment. In the light of these results a qualitative discussion is given of hardness testing, and it is shown both on experimental and on theoretical grounds that with lubricated cones and work-hardened materials the hardness, i.e. load/indentation area, will not depend much on the angle of the cone unless this is less than 10° .

§ 1. INTRODUCTION

WHEN a punch, cone, or sphere or other indenting tool is forced into a ductile material, the load required to form a given indentation will depend on the following factors:

- (a) The shape and size of the indenting tool, and of the specimen if not sufficiently large.
- (b) The coefficient of friction between the indenting tool and the material.
- (c) The yield point and strain-hardening properties of the material, which will depend on temperature and rate of loading.

Up to the present it has proved impossible to develop the mathematical theory of plasticity to the point where it would be possible to calculate the load, and thus any of the conventional hardness numbers, in terms of these factors. In this paper, however, we shall show that it is possible to calculate an approximate value for the load required to force a cylindrical punch deep into a semi-infinite block of ductile material; by deep is meant a penetration equal to four or five times the diameter of the punch. We shall also describe some experiments on static punching into copper blocks designed to test the theory. In the light of these results a general discussion is given of hardness measurement.

§ 2. EXPERIMENTS ON DEEP PUNCHING*

For the material to be indented, blocks of copper, 3.75 in. in diameter and 3.4 in. long were used. The copper was generally in the strain-hardened condition, though one set of measurements was made with annealed copper.

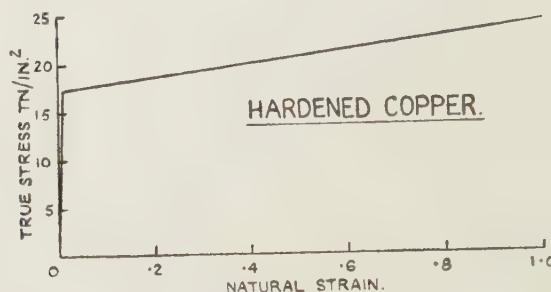


Figure 1.

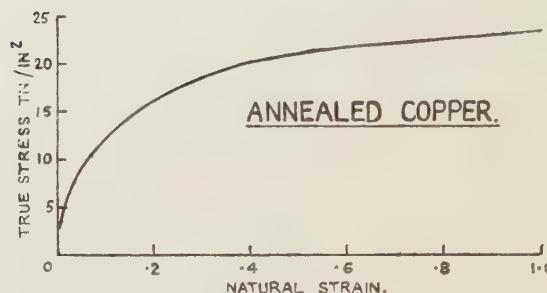


Figure 2.

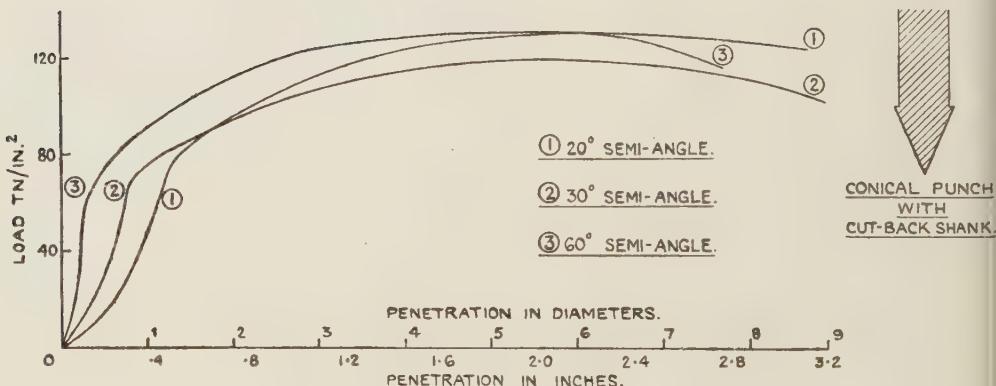


Figure 3. Unlubricated punching into hardened copper.

Stress-strain curves for the copper in compression are shown in figures 1 and 2.† The punches used were 0.350 in. in diameter and had conical heads with semi-angles of 20°, 30° and 60°. The diameters of the parallel parts of the punch

* These experiments were carried out at the Engineering Laboratory of the University of Cambridge under extra-mural contract to the Ministry of Supply.

† For definition of natural strain, cf. equation (1), p. 151.

were made 0.004 inch less than the head diameter; this prevented rubbing of the parallel portion of the punch against the sides of the hole and consequent increase of load due to friction. A diagram of the punch head is shown in figure 3. Punching was carried out at a rate of 1.5 in. per hour approximately.

In figure 3 we show, for the hardened copper, the measured load divided by the cross-sectional area of the punch ($\pi \times 0.175 \times 0.175$ sq. in.). This quantity has the dimensions of a pressure. Figure 4 shows the same quantity

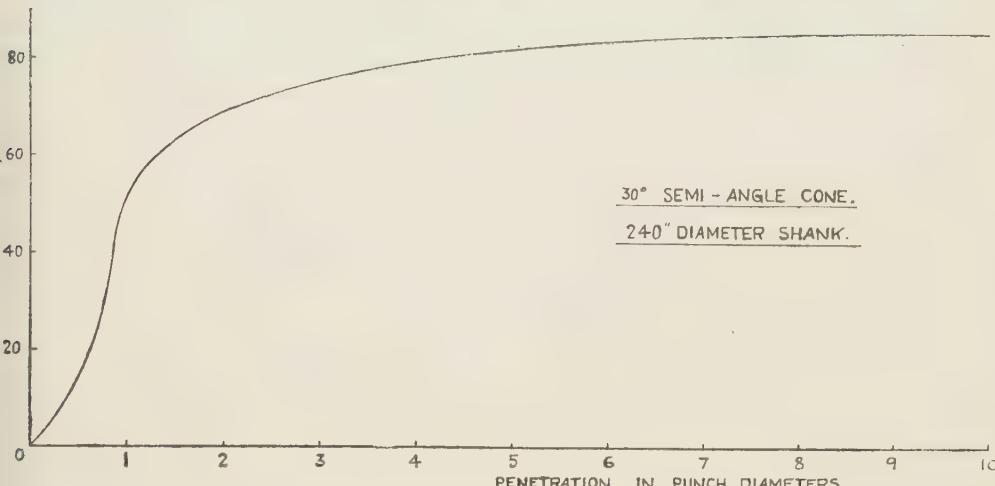


Figure 4. Unlubricated punching into annealed copper.

for annealed copper. It will be seen that as the penetration increases beyond three or four punch diameters, the load tends to a stationary value, which (for the hardened copper) is not markedly different for the three punches. There is some fall-off as the punch approaches the back of the specimen. It is this maximum load which we shall attempt to calculate in the next sections. It is less for annealed than for hardened copper.

§ 3. EFFECTS OF FRICTION

Various attempts to lubricate the surface, and thus to measure the coefficient of friction, were made; the most successful was by rotating the punch at a speed of 100 revolutions an hour. The frictional force would then have acted approximately at right angles to the direction of the punch. Curves showing load against penetration for rotated punches into hardened copper are shown in figure 5. That for the 20° punch shows the greatest tendency to approach a constant load; it was suspected that for the other punches the rotation became unstable and that the shank rubbed against the surface of the hole. The penetrations were continued until the punches fractured.

The difference between the ultimate resistance to penetration with rotated and unrotated conical-headed punches of 20° semi-angle appears from the graphs to be about 45 tons/sq. inch.

It is reasonable to assume that for the high pressures concerned the frictional force s per unit area is independent of pressure, and of the order of the shear stress of the material. The shear stress is $\frac{1}{2}Y$, where Y is the yield stress and

equal to 17.5 tons/sq. in. for the hardened copper used in these experiments. For annealed material s , however, should be rather greater than $\frac{1}{2}Y$, because the copper at the surface will be subject to very considerable cold work.

The frictional force due to the conical portion of a punch of semi-angle θ and cross-sectional area A will then be $As \cot \theta$.

Writing $s \cot 20^\circ = 45$ tons/sq. inch, we find $s = 16.5$ tons/sq. inch.

This value, if correct, leads to the following pressures for the other cones, obtained by subtracting $s \cot \theta$ from the values in figure 3 :

$$\theta = 20^\circ : 130 - s \cot 20^\circ = 85 \text{ tons/sq. inch.}$$

$$\theta = 30^\circ : 119 - s \cot 30^\circ = 91.5 \quad ,$$

$$\theta = 60^\circ : 131 - s \cot 60^\circ = 121 \quad ,$$

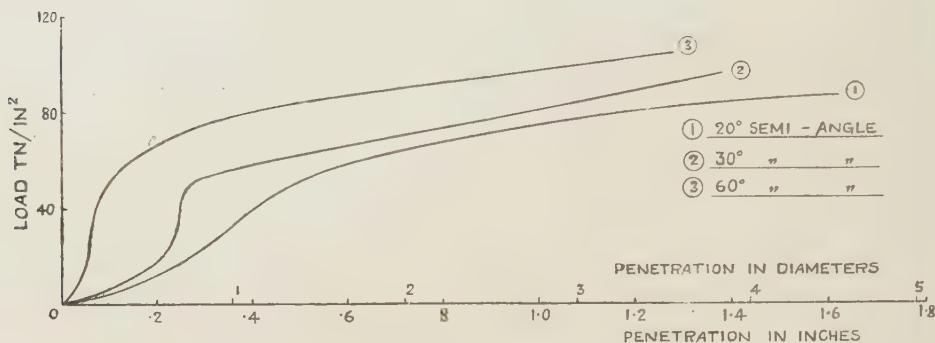


Figure 5. Punching with rotation into hardened copper.

The value for $\theta = 60^\circ$ is probably not significant: it is known that a blunt punch pushes in front of itself a plug which acts effectively as the indenting tool, so that the simple frictional correction described here is not valid. The difference in pressure between the 20° and 30° cones is hardly outside the limits of experimental error.

Since the frictional force is large, the approximation used here of considering it as without effect on the stress component perpendicular to the surface of contact may lead to some error, which, however, we are unable to estimate.

§ 4. THEORETICAL ESTIMATE OF THE LIMITING LOAD

In the last section we have seen how experiments show that the load on a lubricated punch appears to rise to a limiting value, which, for hardened copper, is equal to about five times the yield stress multiplied by the area of the punch; also that this value is not approached until after a penetration of several diameters. In this section we attempt a theoretical estimate of this limiting load.

A full theoretical solution of the equations determining the strains round the head of the punch has not proved possible. Solutions of the following problems can, however, be found:

- (a) Starting with a small hollow sphere in the body of an infinite block of ductile material capable of work-hardening, to determine the pressure p_s which, when applied to the surface of the hole, will enlarge it indefinitely by plastic flow of the material.

(b) Starting with a cylindrical hole of infinite length, to find the pressure p_c that will enlarge the hole indefinitely.

Calculation shows that $p_s > p_c$, but that the difference between them is only about 15 per cent of either. The pressure on a lubricated punch deep in a material is likely to lie between p_s and p_c ; for a very sharp punch (small θ) it should approach p_c , while for a blunt punch the material is pushed away from the head of the punch in much the same way as from the neighbourhood of an expanding sphere, so the pressure should be near to p_s . Thus the fact that p_s and p_c are nearly equal enables rather a close estimate of the limiting load to be made.

We shall now calculate the pressures p_s and p_c .

In both problems we assume that the material has a yield stress Y ; for stresses less than Y the material is assumed to be elastic, with Young's modulus E and Poisson's ratio ν . Above the yield stress we shall assume that in compression the true stress σ is given by

$$\sigma = Y + f(\epsilon), \quad \sigma \geq Y, \quad \dots \dots \dots (1)$$

where ϵ is the natural strain, given by

$$\epsilon = \log_e \left(\frac{\text{final area of cross-section}}{\text{initial area of cross-section}} \right).$$

At any stage in the expansion of the spherical and cylindrical hole we denote the radius of the hole by a , and the radius of the plastic region surrounding it by c . Within the plastic region we shall neglect all volume changes.

We shall show below that

$$\begin{aligned} \frac{c}{a} &= \left\{ \frac{E}{(1+\nu)Y} \right\}^{\frac{1}{2}} && \text{Spherical hole} \\ &= \left\{ \frac{\sqrt{3}E}{2(1+\nu)Y} \right\}^{\frac{1}{2}} && \text{Cylindrical hole} \end{aligned} \quad \dots \dots \dots (2)$$

Thus as the hole expands the ratio of the radius of the plastic region to that of the hole remains constant.

In order to progress further with our problem it is necessary to make some assumption about the stress-strain relation in the plastic region for a more general case than simple tension or compression. Following Nadai (1937), we shall assume that the octahedral stress is a definite function of the octahedral shear strain for all strain configurations; this is at any rate likely to be the case when, as here, the principal axes of stress and strain in a given element coincide and do not rotate during plastic flow. The octahedral stress τ_n is defined by the equation

$$\tau_n = \frac{1}{3} \{ (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 + (\sigma_1 - \sigma_2)^2 \}^{\frac{1}{2}}, \quad \dots \dots \dots (3)$$

and the octahedral natural shear strain γ_n by the differential relation

$$d\gamma_n = \frac{2}{3} \{ (d\epsilon_2 - d\epsilon_3)^2 + (d\epsilon_3 - d\epsilon_1)^2 + (d\epsilon_1 - d\epsilon_2)^2 \}^{\frac{1}{2}}, \quad \dots \dots \dots (4)$$

where $\sigma_1, \sigma_2, \sigma_3$ are the principal stresses and $\epsilon_1, \epsilon_2, \epsilon_3$ are the principal natural strains. In a tensile or compression test

$$\tau_n = \sqrt{2\sigma/3}, \quad \gamma_n = \sqrt{2\epsilon};$$

the universal relation between τ_n and γ_n then follows from (1) and is

$$\frac{3}{\sqrt{2}} \cdot \tau_n = Y + f \left(\frac{\gamma_n}{\sqrt{2}} \right); \quad \tau_n \geq \frac{\sqrt{2}Y}{3}. \quad \dots \dots \dots (5)$$

In our cylindrical problem, let σ_r , σ_θ be the radial and tangential stresses. Following Nadai, we set for σ_z in the plastic region

$$\sigma_z = \frac{1}{2}(\sigma_r + \sigma_\theta).$$

This clearly follows from the assumptions of plane strain and no volume change. We thus obtain from (3)

$$\tau_n = \frac{1}{2} \sqrt{\frac{3}{2}} \cdot (\sigma_\theta - \sigma_r).$$

Also, since the z component of strain is zero and $(\epsilon_\theta + \epsilon_r)$ vanishes by our assumption of no volume change,

$$\gamma_n = 2\sqrt{\frac{2}{3}} |\epsilon_r|.$$

It therefore follows from (5) that the stress-strain relation is

$$\sigma_\theta - \sigma_r = \frac{2Y}{\sqrt{3}} + \frac{2}{\sqrt{3}} f \left\{ \frac{2}{\sqrt{3}} |\epsilon_r| \right\}; \quad \sigma_\theta - \sigma_r \geq \frac{2Y}{\sqrt{3}}. \quad \dots \dots \dots (6)$$

In the boundary of the plastic region

$$\sigma_\theta - \sigma_r = \frac{2Y}{\sqrt{3}}. \quad \dots \dots \dots (7)$$

This is the usual Mises condition for plasticity.

If we integrate the condition of equilibrium, namely

$$\frac{d\sigma_r}{dr} = \frac{\sigma_\theta - \sigma_r}{r}, \quad \dots \dots \dots (8)$$

throughout the plastic region from $r=a$ to $r=c$, we obtain for the pressure p_c on the boundary of the hollow cylinder (the value of $(-\sigma_r)$ at that point)

$$p_c = \frac{Y}{\sqrt{3}} \left(1 + 2 \log \frac{c}{a} \right) + \frac{2}{\sqrt{3}} \int_a^c f \left\{ \frac{2}{\sqrt{3}} |\epsilon_r| \right\} \frac{dr}{r}. \quad \dots \dots \dots (9)$$

To evaluate the integral we need an expression for ϵ_r . If an element at radius r in the plastic region when the hole is of radius a was formerly at radius s when the hole was of zero radius, then

$$r^2 = a^2 + s^2$$

and

$$\epsilon_r = -\epsilon_\theta = -\log(r/s).$$

Thus (9) becomes

$$p_c = \frac{Y}{\sqrt{3}} \left(1 + 2 \log \frac{c}{a} \right) + \frac{2}{\sqrt{3}} \int_a^c f \left\{ \frac{2}{\sqrt{3}} \log \frac{r}{\sqrt{r^2 - a^2}} \right\} \frac{dr}{r}. \quad \dots \dots \dots (10)$$

The evaluation of the integral will be carried out in the next section.

We have next to find the value of c/a ; to do this we equate the plastic and elastic displacements (denoted by u) on the plastic-elastic boundary. The assumption of no volume change in the plastic region gives, for the displacement on the boundary of the plastic region,

$$u = a^2/2c,$$

On the boundary of the elastic region the assumption that $\sigma_\theta - \sigma_r = 2Y/\sqrt{3}$ gives

$$u = (1 + \nu) Y c / \sqrt{3} E.$$

Equating these gives

$$\frac{c^2}{a^2} = \frac{\sqrt{3} E}{2(1 + \nu) Y}. \quad \dots \dots (11)$$

A similar analysis applies to the expansion of a spherical hole; it is found that

$$\tau_n = \sqrt{2} (\sigma_\theta - \sigma_r)/3,$$

and, since $\epsilon_r + 2\epsilon_\theta = 0$,

$$\gamma_n = 2\sqrt{2} \cdot \log(r/s).$$

It follows that

$$\sigma_\theta - \sigma_r = Y + f\{2 \log(r/s)\}.$$

The condition at the plastic-elastic boundary is now

$$\sigma_\theta - \sigma_r = Y,$$

and the equilibrium equation

$$\frac{d\sigma_r}{dr} = \frac{2(\sigma_\theta - \sigma_r)}{r}.$$

On integrating the latter equation we obtain

$$p_s = \frac{2Y}{3} \left(1 + 3 \log \frac{c}{a} \right) + 2 \int_a^c f \left(2 \log \frac{r}{(r^3 - a^3)^{\frac{1}{2}}} \right) \frac{dr}{r}, \quad \dots \dots (12)$$

where

$$\frac{c^3}{a^3} = \frac{E}{(1 + \nu) Y}.$$

§ 5. EVALUATION OF INTEGRALS

The true-stress natural-strain curve for many materials becomes straight at large strains (*cf.* MacGregor and also figure 2). Figure 7 shows the tensile curve for mild steel (MacGregor, *loc. cit.*). For work-hardened materials the whole of the curve above the elastic limit is often approximately linear (*cf.* figure 1), and we can therefore write in this case

$$f(\epsilon) = A\epsilon.$$

We then have, for the second term in (10), which represents the contribution to the pressure from the cold work,

$$\frac{4A}{3} \int_a^c \log \left[\frac{r}{\sqrt{(r^2 - a^2)}} \right] \frac{dr}{r}.$$

This reduces to

$$-\frac{A}{3} \left[\sum_1^\infty \frac{1}{n^2 t^{2n}} \right]_1^{c/a}$$

and, if terms in a^2/c^2 are neglected in comparison with unity, to

$$A\pi^2/18.$$

In the general case where the strain-hardening curve is not linear, we shall suppose that above some value ϵ_0 of the strain

$$f(\epsilon) = Y' + A\epsilon; \quad \epsilon > \epsilon_0.$$

A short calculation gives for the second term in (10)

$$\frac{A\pi^2}{18} + \frac{Y'y_0}{\sqrt{3}} \tau \frac{1}{\sqrt{3}} \int_{y_0}^{2 \log(c/a)} \left[f \left\{ \frac{1}{\sqrt{3}} \log \frac{e^y}{e^y - 1} \right\} - \frac{A}{\sqrt{3}} \log \frac{e^y}{e^y - 1} \right] dy,$$

where

$$y_0 = \sqrt{3}\epsilon_0 - \log(e^{\sqrt{3}\epsilon_0} - 1).$$

In a similar way we find for the spherical hole the contribution to p_s from the strain hardening is

$$\frac{2A\pi^2}{27} + \frac{2Y'y_0}{3} + \frac{2}{3} \int_{y_0}^{3 \log(c/a)} \left[f \left\{ \frac{2}{3} \log \frac{e^y}{e^y - 1} \right\} - \frac{2A}{3} \log \frac{e^y}{e^y - 1} \right] dy,$$

where

$$y_0 = \frac{3}{2}\epsilon_0 - \log(e^{3\epsilon_0/2} - 1).$$

§ 6. NUMERICAL VALUES

We thus see that for a material for which true stress σ and natural strain ϵ are connected by the relation

$$\sigma = Y + A\epsilon,$$

the pressure p_c to enlarge a cylindrical hole is given by

$$p_c = \frac{Y}{\sqrt{3}} \left(1 + 2 \log \frac{c}{a} \right) + \frac{\pi^2}{18} A,$$

with

$$\frac{c}{a} = \left(\frac{\sqrt{3}E}{2(1+\nu)Y} \right)^{\frac{1}{3}}, \quad \dots \dots \quad (13)$$

and for a spherical hole

$$p_s = \frac{2Y}{3} \left(1 + 3 \log \frac{c}{a} \right) + \frac{2\pi^2}{27} A,$$

with

$$\frac{c}{a} = \left(\frac{E}{(1+\nu)Y} \right)^{\frac{1}{3}}.$$

Numerical values are as follows : a typical stress-strain curve for mild steel is shown in figure 7. For this material $(c/a)_{\text{cylinder}} = 22$, $(c/a)_{\text{sphere}} = 8$. In spite of this wide difference, p_c and p_s are nearly equal; in tons/sq. inch,

$$p_c = 100, \quad p_s = 120,$$

the contributions from work-hardening being 29 and 30% in the two cases. Y was taken to be 17 tons/sq. in.

For the cold-worked copper used in the experiments described in sections 2 and 3, similar results are valid, only here the contribution from cold-work is smaller. We took

$$Y = 17.5, \quad A = 6.5, \quad E = 8000,$$

all in tons/sq. inch. ν was not measured, but was assumed to be 0.34. Calculation then gave

$$p_c = 71.3 \quad (3.6 \text{ due to cold work}),$$

$$p_s = 84.5 \quad (4.8 \text{ due to cold work}).$$

It will be noticed again that the values do not differ much. The values of c/a were 17 and 7 respectively.

For the annealed copper shown in figure 2, we found $p_c = 43$ and $p_s = 52$ tons/sq. in.

§ 7. COMPARISON WITH STATIC PUNCHING

As already emphasized, we expect the pressure on the head of a punch several diameters deep in the hardened copper to lie between p_c , representing a very sharp punch, and some value below p_s , representing a blunt one (provided friction is eliminated). As explained in section 3, we do not consider the allowance made for friction sufficiently certain to distinguish experimentally between sharp and blunt punches. For a lubricated 20° semi-angle cone our measured value was 85 tons/sq. in., which lies close to our calculated value of P_s , namely 84.5.

For annealed copper, our calculated pressure (between 43 and 52) comes out considerably less than that measured for an unlubricated punch (84 tons/sq. inch). If we ascribe this to a frictional force s per unit area, and take 52 to be the pressure for a lubricated punch, then $52 + s \times 1.73 = 84$, giving $s = 18.5$ tons/sq. inch, which is about the same as we found for hardened copper. Experiments with rotated punches in annealed materials would be of interest. It is perhaps to be expected that the frictional forces on annealed and hardened copper would be about equal to the shear stress of the latter, since the copper near the surface of contact must be highly cold-worked.

§ 8. SURFACE EFFECTS IN PUNCHING

As figures 3, 4 and 5 show, the load on a punch does not reach its maximum value as soon as the head is embedded in the material, but continues to rise while the penetration increases by several diameters. The same is true of the effective mean pressure on the punch, defined as load divided by the momentary area of the hole on the front surface. The graphs of mean pressure against penetration for the rotated and unrotated 20° S.A. cone are shown in figure 6. On a dimensional argument the pressure will be constant while the conical head is going in. The experimental results do not give such a constant pressure, and the discrepancy is due to an error in the zero measurement of penetration—an error which is proportionately less as the penetration increases. For this reason the straight-line part of the curve is an extrapolation from the results after the head is entirely in the copper.*

It is sometimes stated that the increase in pressure after entry of the head is due only to the strain-hardening of the metal; this is certainly not true, and would take place if the material did not work-harden at all. The region which is plastic round the head of a punch deep in a material must be very extensive, of width between 7 and 17 punch diameters in the case of copper according to the arguments of section 4. Near the surface, however, the constraint on the copper is less, and it can escape by forming a lip round the hole, which is very marked with lubricated punches. Less work per unit volume is therefore done in making the hole. Clearly the small contribution to the maximum pressure by the cold work, calculated in section 6, by no means accounts for the rise in mean pressure from 45 to 85 tons/sq. in. for the rotated 20° punch.

* This constant pressure for the rotated cone is in close agreement with the value obtained by lubrication and repeated loading. See section 9 and figure 8.

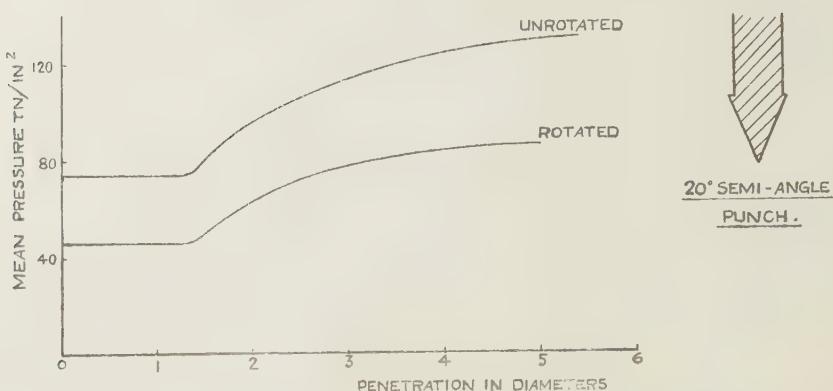


Figure 6. Pressure-penetration curves for 20° semi-angle cone punching into hardened copper.

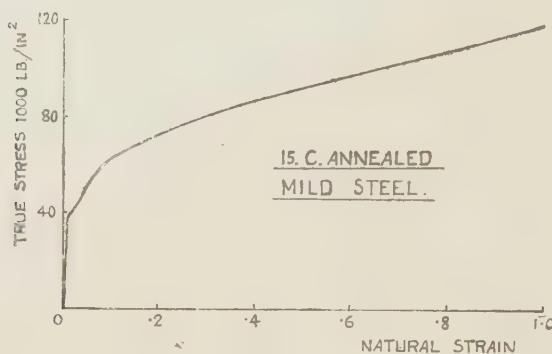


Figure 7.

(Taken from a paper by C. W. MacGregor in the Timoshenko Anniversary Volume.)

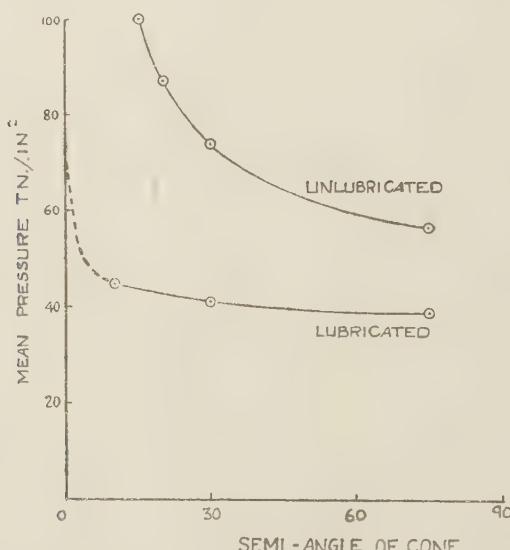


Figure 8. Indentation tests with cones on hardened copper.

Hardness contours taken over a cross-section of a block of annealed copper after punching are shown in figure 9. They imply a smaller diameter of plastic flow near the surface than in the body of the block, as is expected from the

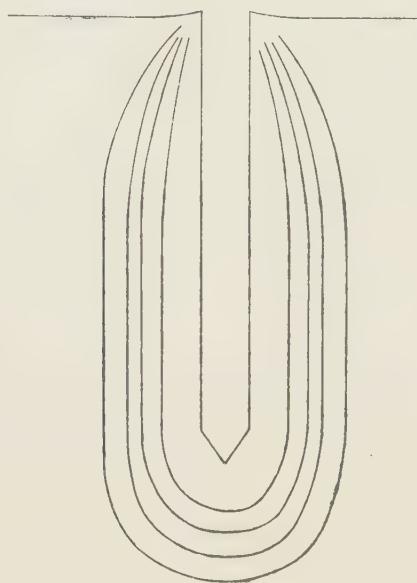


Figure 9. Hardness contours after punching into annealed copper.

discussion given above. Moreover, the actual extent of plastic flow when the punch is beginning to penetrate is still less, since some of the flow near the surface is caused during the later stages of the penetration.

§ 9. INDENTATION HARDNESS TESTS

Hardness tests with conical indenting tools are particularly suitable for theoretical discussion, because the ratio of load to surface impression area must, on dimensional grounds, be independent of load. Tests with lubricated punches are the simplest to interpret. Such tests have been made by various authors (*cf.* Hankins, 1925 and 1926). In figure 8 we show some results obtained in the Cambridge Engineering Laboratory with lubricated and unlubricated conical punches in strain-hardened copper (with a stress-strain curve as in figure 1). The punches were solid steel cones and the lubricant (graphite grease) was applied repeatedly as the load was increased; at a given load, lubrication was continued until there was no further increase in the diameter of the indentation.

It will be seen that for the lubricated punches, the mean pressure defined by load/(surface area of indentation) increases slightly with decreasing cone angle, and is about 40 tons/sq. inch. (The opposite is the case when the head of the punch is far from the surface, the mean pressure decreasing with decreasing angle). We conclude that for this material the hardness measured with a lubricated conical punch depends little on the head shape and is about half the experimental ultimate pressure for deep punching (85 tons/sq. in.). Whether this is so for annealed materials will be discussed below.

We consider, on theoretical grounds, that for a cone of sufficiently small angle, the resisting pressure must tend to some value near that for a cylindrical punch or, more exactly, to the theoretical value p_c for the enlargement of a long cylindrical hole. In figure 8, therefore, we have extrapolated the experimental curve for lubricated cones to 71 tons/sq. inch for zero semi-angle (the theoretical value of p_c calculated in section 6). It is to be expected that only for cones of semi-angle less than 10° will these high values be reached. The explanation is to be found in the variation of pressure along the cone, increasing towards the tip, where the confinement is most severe. For example, even a 10° S.A. cone has a penetration of only between 3 and 4 times the impression diameter, whereas we know from deep punching that the maximum pressure is not attained until after 4 diameters penetration. Experiments with sharp cones in a material soft enough to insert them without breaking would be of interest.

The variation in mean pressure with cone angle, small though it is, is an important consideration in the type of experiment where different cones are used to evaluate the coefficient of friction. The calculation based on the experimental values usually involves the subtraction of nearly equal quantities, and so neglect to allow for change of pressure with angle can give completely false results for the friction.

For an indenter with a shape such that the ratio (impression diameter)/(penetration) decreases with depth, the mean pressure steadily increases with penetration for the reasons discussed in section 8. This will be so, for example, in the Brinell test with spheres (where by pressure is meant, as usual, load/(impression area), not load/(spherical area)). This is confirmed experimentally by the empirical result usually referred to as Meyer's law. This states that the load L on a ball is proportional to d^n , where d is the impression diameter and n is greater than 2. According to the ideas of this paper, n should be slightly greater than 2 even for a material which does not show work-hardening.

Empirically n is largest for annealed materials and least for severely strain-hardened materials. It is clear from general considerations that this should be so, as pointed out in various papers at a discussion held by the Institution of Mechanical Engineers. For a shallow indentation by a sphere, or an indentation by a very blunt cone, no part of the material will be highly strained. For a deep penetration by a sphere, or penetration by a sharp cone, large strains will be involved; work-hardening will thus take place.

We therefore expect that for an annealed material the pressure on a lubricated conical punch would rise more rapidly with decreasing cone angle than shown in figure 8. While (in terms of the yield stress) the value for the 90° cone would be unaffected, that for the 0° cone would be increased by work-hardening as calculated in formulae (12). Experiments with an annealed material would be of interest.

As regards the limiting pressure for blunt cones ($\theta = 90^\circ$) shown in figure 8, it is of interest to compare this with the theoretical value obtained by Hencky (1923) by a very approximate method, according to which yield with a cylindrical flat-headed punch should begin when $p = 2.8Y$. Since Y was 17.5 tons/sq. inch, Hencky's formula gives 49 against the observed value of 39 tons/sq. inch.

Various empirical rules have been given from time to time in order to estimate the tensile yield stress from a hardness test. It is clear that no general conversion factor can be laid down, even for the same material, since the factor will depend largely on the amount of pre-working. But for severely cold-worked metals there seem to be good reasons for supposing a constant conversion factor to exist independent of the material tested, with the proviso that the impression diameter must be the same in every case. In this way it is possible to eliminate the effect of variation of mean pressure with penetration, since the variation will then be the same for all the materials tested. A second precaution is the elimination of friction. The only variables on which the conversion factor can now depend are the yield stress and elastic constants (for the same indenter). The elastic properties are probably of not more than minor importance since we know that in a cold-worked metal the material escapes from the indenter into the lip.

In these circumstances the mean pressure will probably be between two and three times the yield stress of the worked metal, depending on the geometry of the indentation. For the cones indenting the hardened copper of yield strength 17.5 tons/sq. inch the pressure was about 40 tons/sq. inch, giving a ratio of 2.3.

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AN EXPERIMENTAL INVESTIGATION OF EXTRAPOLATION METHODS IN THE DERIVATION OF ACCURATE UNIT-CELL DIMENSIONS OF CRYSTALS

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ABSTRACT. Measurements on x-ray photographs of cylindrical specimens of different absorption and thickness taken in a camera without eccentricity show that the absorption error in the apparent unit-cell dimension a is proportional to

$$\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}.$$

The plot of a against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ is linear down to $\theta = 30^\circ$ for all four specimens used. The extrapolated values for a are in good agreement, and this extrapolation function is accordingly recommended in the case of data from well constructed cameras. Other extrapolation functions are also considered, and the effect of various sources of error discussed. A table of $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ is given.

§ 1. INTRODUCTION

IN the determination of accurate unit-cell dimensions from powder photographs, three sources of systematic error are usually considered, due to

- (a) absorption of the x-ray beam in the specimen;
- (b) the displacement of the rotation axis of the specimen relative to the geometric centre of the cylindrical film, usually called the *eccentricity error*;
- (c) inaccurate determination of the camera constants.

It may be shown that errors due to these three causes vanish at $\theta = 90^\circ$, which corresponds to extreme back-reflection along the path of the incident beam. The procedure usually adopted, therefore, is to derive apparent cell dimensions a from a number of lines on the photograph, to plot these values against some function of the Bragg angle θ , and to extrapolate to a value corresponding to $\theta = 90^\circ$.

Some uncertainty exists as to the best function of θ to use in order to obtain a linear extrapolation. Current practice is to plot a against $\cos^2 \theta$ for high-angle lines only (i.e. those with clearly resolved α -doublets) and to extrapolate linearly to $\cos^2 \theta = 0$. It appears that this function has been chosen because the eccentricity error $\left(\frac{\delta a}{a} \right)_{\text{ecc}}$ is easily shown to be proportional to $\cos^2 \theta$. The absorption

error $\left(\frac{\delta a}{a}\right)_{\text{abs}}$, however, is not proportional to $\cos^2\theta$. Various workers, on theoretical grounds, have derived different functions relating $\left(\frac{\delta a}{a}\right)_{\text{abs}}$ and θ . Thus

1. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \frac{\cos^2\theta}{\theta}$ Bradley and Jay (1932).
2. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \frac{\cos^2\theta}{\sin\theta}$ Jay (1944).
3. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \cot\theta \cos^2\theta$ Buerger (1942).
4. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \right)$ Taylor and Sinclair (1944).*

The use of a $\cos^2\theta$ plot assumes that, whatever the nature of the absorption error function, it can be approximately represented by $\cos^2\theta$ at high angles. It is not always possible, however, to obtain a sufficient number of lines at angles high enough for this to be true, and we have carried out the work described here in order to obtain experimental evidence concerning the best extrapolation function for general use.

§ 2. EXPERIMENTAL

The camera used was the 19-cm. diameter high-temperature camera designed and described by Wilson (1941), the film being in two halves. The design minimizes the possibility of eccentricity, and after consultation with Mr. C. E. Chapman, who made the instrument, we satisfied ourselves that effectively no eccentricity could be present. The camera angle, θ_k , has been very carefully measured by Wilson and Lipson (1941), who discussed possible errors in this connection. In effect, then, we have used an excellently constructed and calibrated camera to investigate the *absorption error*, eccentricity and calibration errors being absent. The method of film measurement described by Lipson and Wilson (1941) avoids errors due to uniform film shrinkage, but requires an accurate value for the camera angle. We therefore thought it instructive to do some calculations using camera angles in error by a known amount.

For simplicity, the substance photographed should be cubic and give a large number of reasonably strong and sharp lines over a wide range of θ values. We chose the γ -structure Cu_9Al_4 , which, with Cu radiation, gives a well resolved and intense α -doublet ($h^2 + k^2 + l^2 = 126$) at $\theta_{\alpha_1} = 83^\circ 4 : \theta_{\alpha_2} = 84^\circ 8$, together with a large number of lines going down to the lowest order line measurable ($h^2 + k^2 + l^2 = 6$) with $\theta = 12^\circ 7$. Table 1 gives a list of the lines measured, which will be seen to be distributed fairly evenly over the photograph. The Cu radiation was filtered to avoid the confusion inevitable with β -lines in a pattern of this complexity. The specimens were accurately centred and rotated during the exposure. The temperature for each exposure was kept constant by circulating water through the cooling jacket of the camera. Care was taken to ensure that the electron beam in the Metropolitan-Vickers x-ray tube was homogeneously

* Subsequently to our work.

Table 1
X-ray reflections from Cu₉Al₄; CuK α radiation
(Approximate θ values from thick diluted specimen)

$h^2 + k^2 + l^2$	θ	$h^2 + k^2 + l^2$	θ	$h^2 + k^2 + l^2$	θ
6	12·8	66 _{a1}	46·2	102 _{a2}	63·8
9	15·7	66 _{a2}	46·3	108 _{a1}	67·0
12	18·2	72 _{a1}	48·9	108 _{a2}	67·3
14	19·7	72 _{a2}	49·0	114 _{a1}	71·0
18	22·4	76 _{a1}	50·7	114 _{a2}	71·4
22	24·8	78 _{a1}	51·6	118 _{a1}	74·1
24	26·0	90 _{a1}	57·3	120 _{a1}	75·9
36 _{a1}	32·3	90 _{a2}	57·5	120 _{a2}	76·4
48 _{a1}	38·1	98 _{a1}	61·3	122 _{a1}	77·9
54 _{a1}	40·8	98 _{a2}	61·6	126 _{a1}	83·4
54 _{a2}	40·9	102 _{a1}	63·5	126 _{a2}	84·8

distributed over the target, i.e. no "hot-spots" were present. The camera was adjusted so that its slit-system made a small angle with the face of the target, thus securing a "foreshortened" circular focal spot, and this arrangement was accurately reproduced for each exposure.

§ 3. SPECIMENS USED

Filings of Cu₉Al₄ were annealed at 650° for $\frac{1}{2}$ hour and sieved through a 350 B.S.S. mesh. This sample was used to prepare specimens (*a*) and (*b*) described below. Specimens (*c*) and (*d*) were prepared from the same filings annealed at a slightly higher temperature, 700°, for $\frac{1}{2}$ hour.

Four specimens were prepared :

- (*a*) A rod 0·59 mm. diameter made by rolling with gum tragacanth.
- (*b*) As above, 1·46 mm. diameter.
- (*c*) A silica tube, bore 0·45 mm., uniform wall thickness 0·025 mm., filled with Cu₉Al₄ powder packed as densely as possible.
- (*d*) A Lindemann-glass tube, bore 1·35 mm., uniform wall thickness 0·016 mm., filled as above.

The use of gum tragacanth may be unfamiliar and will be described. The specimens are made by mixing the specimen powder with gum tragacanth powder, moistening, and rolling the resulting dough into a uniform rod. When dry, this rod is quite rigid. Specimen (*a*) was the thinnest one it was convenient to make with this technique, and was prepared with enough gum tragacanth roughly to satisfy the generally accepted condition for ensuring good photographs, namely, that $\mu r = 1$, where μ = linear absorption coefficient of the specimen mixture, r = radius of specimen, the gum tragacanth acting as a diluent. Specimen (*b*) was prepared from the same mixture but was deliberately made very thick; the condition $\mu r = 1$, of course, no longer applied. Specimens (*c*) and (*d*) approximated in density and absorption to a wire specimen. Here again one specimen was made as thin as possible and the other very thick. It should be pointed out

that each of our specimens was a homogeneous solid cylinder. The method of preparing specimens by causing the powdered sample to adhere to the surface of a hair or a thin glass fibre gives a hollow cylinder.

§ 4. EXTRAPOLATIONS

The results for specimen (b) (the thick gum tragacanth specimen) were considered in some detail. The apparent a values were plotted against the following functions of θ :

$$\theta^\circ, \cot \theta, \cos^2 \theta, \cot \theta \cdot \cos^2 \theta, \cot \theta \left(\frac{1 + \cos^2 \theta}{2} \right).$$

$$\frac{\cos^2 \theta}{\sin \theta}, \quad \frac{\cos^2 \theta}{\theta}, \quad \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right).$$

These plots are shown in figure 1, and display several interesting features.

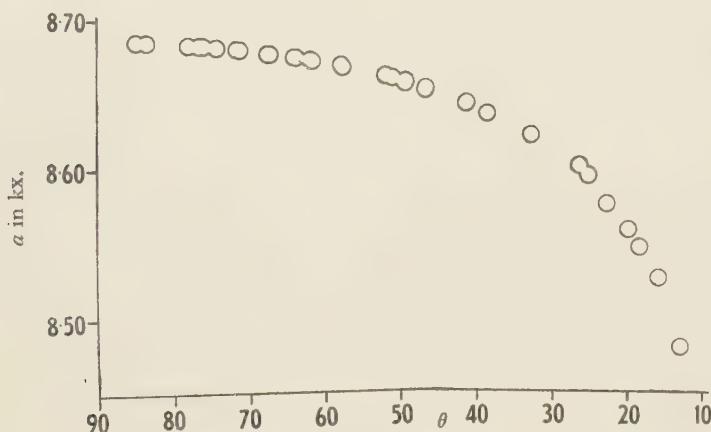


Figure 1 a.

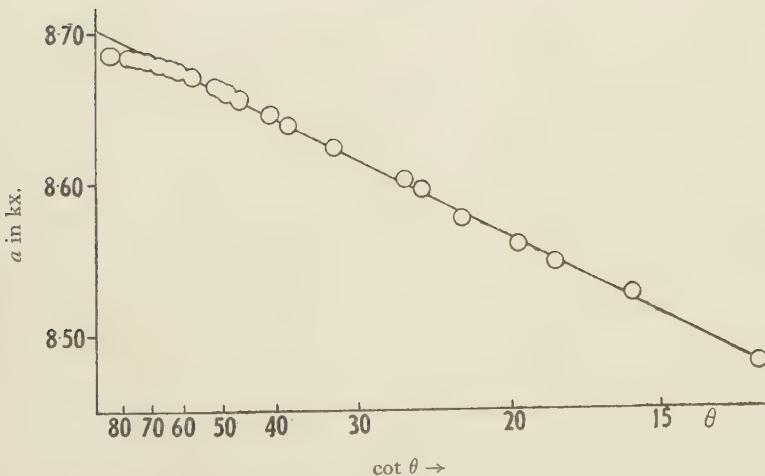


Figure 1 b.

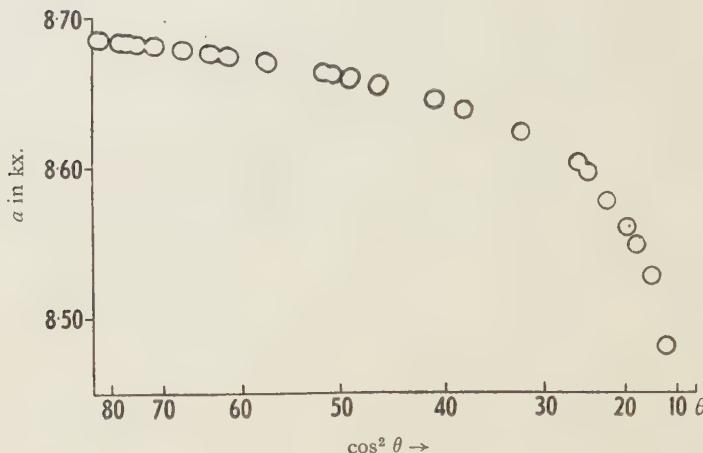


Figure 1 c.

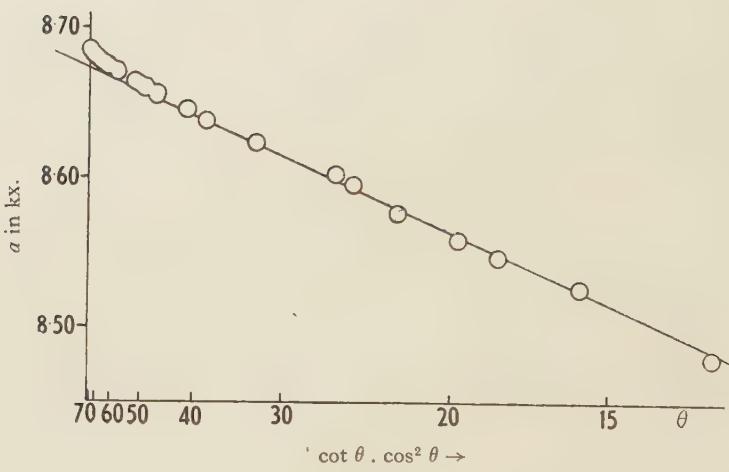


Figure 1 d.

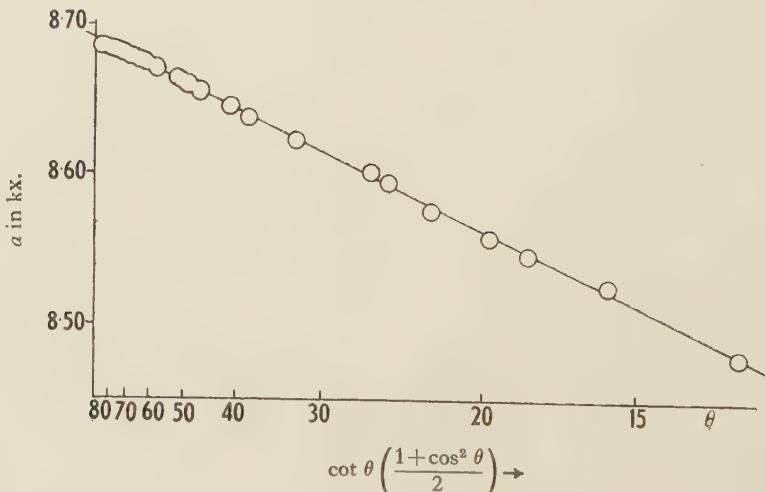


Figure 1 e.

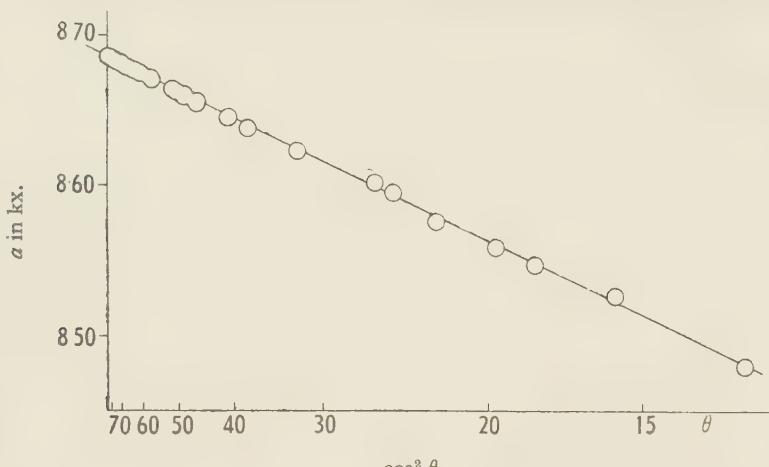


Figure 1 f.

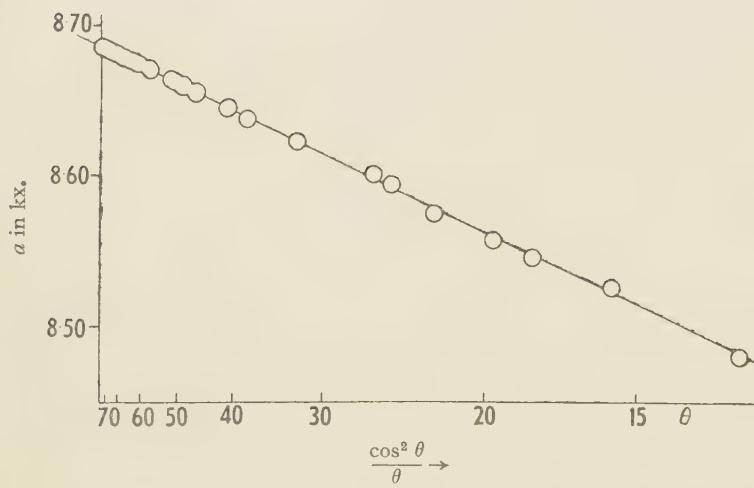
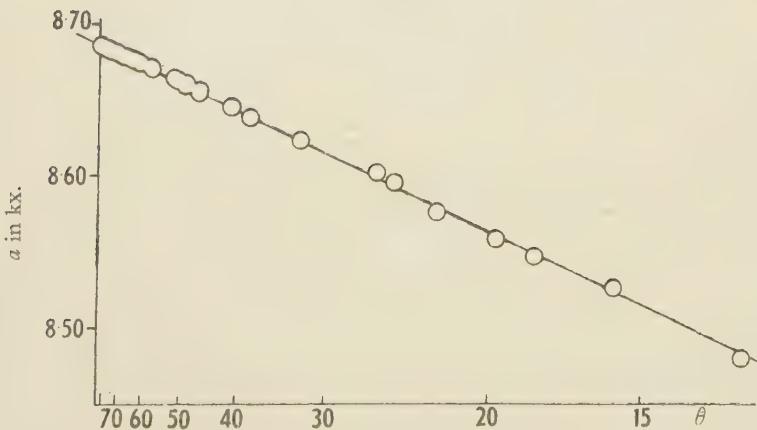


Figure 1 g.



$$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \rightarrow$$

Figure 1 h.

Figure 1. Thick diluted specimen.
Plots of a against various functions of θ .

Firstly, the $\cos^2 \theta$ plot is nearly linear only over a very small range, and its main advantage over the straightforward plot against θ is the way in which it compresses the high angle values towards $\cos^2 \theta = 0$. Secondly, it is clear that the plot must be against $\cot \theta$, or against a very similar function, if linearity over the whole range is to be achieved. The plot against $\cot \theta$ itself shows a falling off from linearity at high angles, while the use of $\cot \theta \cos^2 \theta$ (Buerger's absorption-error plot) gives the opposite deviation. A plot against the arithmetic mean of these two functions, $\cot \theta \frac{1 + \cos^2 \theta}{2}$, shows a marked improvement but still falls off at high angles. The plot against $\frac{\cos^2 \theta}{\sin \theta}$ (or $\cot \theta \cos \theta$, the geometric mean) is apparently linear, as is the plot against the very similar function $\frac{\cos^2 \theta}{\theta}$. A close examination of the two extrapolations, however, shows that in the case of the $\frac{\cos^2 \theta}{\sin \theta}$

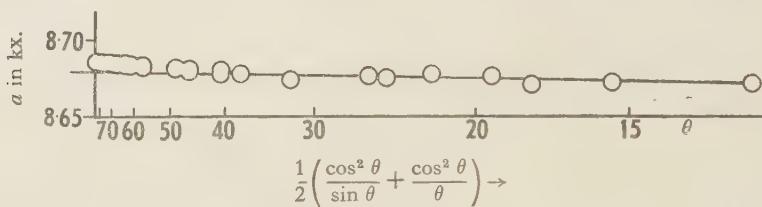


Figure 2 a.

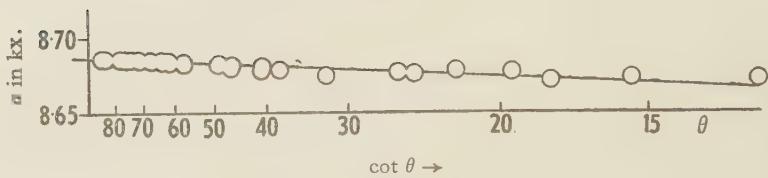


Figure 2 b.

Figure 2. Medium thickness diluted specimen.

plot the best straight line drawn through the high-angle points only has a slightly smaller slope than the best straight line drawn through all the points, whereas the reverse is true for the $\frac{\cos^2 \theta}{\theta}$ plot. In conformity with these observations, a remarkably good linear plot is obtained against the arithmetic mean of these functions, $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$. In this case the best overall extrapolation coincides exactly with the best high-angle extrapolation, as is shown more clearly in the larger scale drawing in figure 5 a (lower plot).

The results for specimen (a), the gum tragacanth specimen of medium thickness, are not in agreement with these findings. The plot against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ is not linear over the whole range (figure 2 a). The high-angle points fall closely on a straight line, but the slope of this line is markedly greater than that of the line drawn through the low-angle points. The latter extrapolation,

it is interesting to note, is almost horizontal. The plot against $\cot \theta$, on the other hand, is linear over the whole range (figure 2 b).

The thick undiluted specimen (*d*) gives similar results to those obtained with specimen (*b*). Plotting against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ gives a remarkably good straight line over the whole range (figure 3).

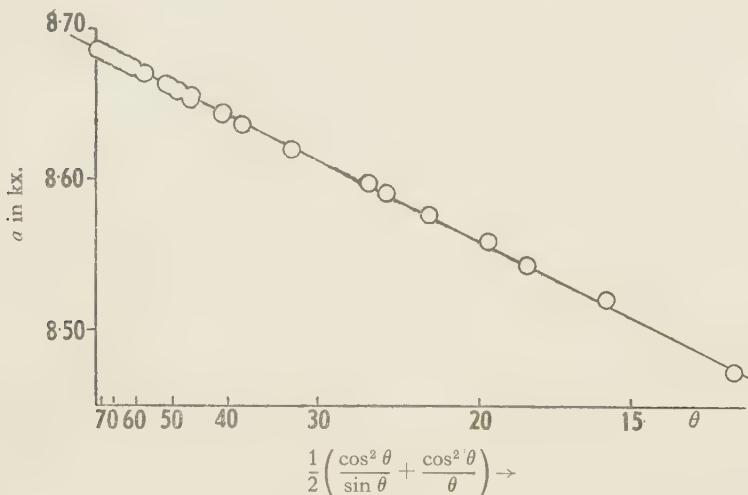


Figure 3. Thick undiluted specimen.

The undiluted specimen of medium thickness, specimen (*c*), behaves similarly to specimen (*a*). The plot against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ is not linear over the whole range, although a good straight-line extrapolation can be obtained with the high-angle points (figure 4 *a*). The linearity of the plot against $\cot \theta$ (figure 4 *b*) is not as good as with specimen (*a*), as there is a slight downwards bend at high angles. A plot against the arithmetic mean of the two functions is nearly linear over the whole range, but is unsuitable for extrapolation.

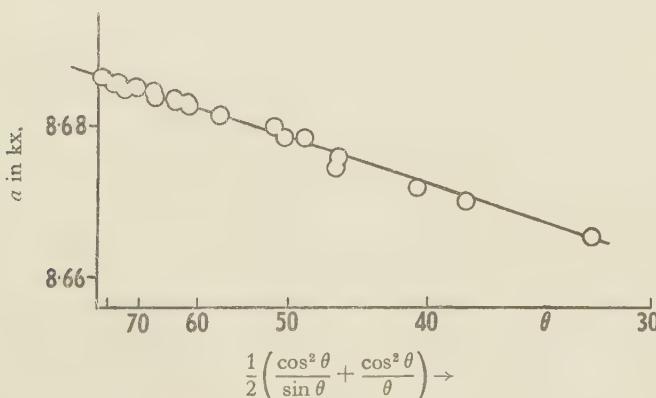


Figure 4 a.

Large scale plot of a against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ for lines with $\theta > 30^\circ$.

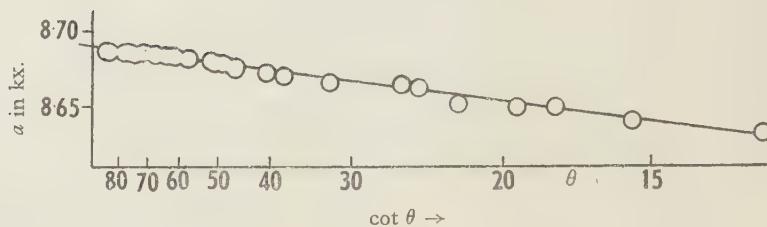


Figure 4 b.

Figure 4. Medium thickness undiluted specimen.

These results are summarized in the following table :

Specimen	Best overall plot for linearity	Best high-angle plot for accuracy	Low-angle limit of linearity for high- angle plot (θ)
(a) Medium thickness diluted	$\cot \theta$	$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$	30°
(b) Very thick diluted	$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$	„	(13°)*
(c) Medium thickness undiluted	$\frac{1}{2} \left[\cot \theta + \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \right]$	„	30°
(d) Very thick undi- luted	$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$	„	(13°)*

* For line 6, the lowest line measured. The true limit may be lower than this.

We interpret these results in the following way. Two factors are contributing to the errors in the apparent a values, (a) the absorption, and (b) systematic observational errors.

(a) The absorption error

$$\left(\frac{\delta a}{a} \right)_{\text{abs}} \propto \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}.$$

This is in agreement with the theoretical finding of Taylor and Sinclair for the case of an "exponential" focus, although we had established the relation experimentally before they had reached this conclusion.

(b) Errors in a due to systematic observational errors in measuring θ are proportional to $\cot \theta$. This is easily confirmed by differentiating the Bragg equation :

$$a = \frac{\lambda}{2} \sqrt{h^2 + k^2 + l^2} \operatorname{cosec} \theta \quad (\text{for a cubic crystal});$$

therefore $\delta a = -\frac{\lambda}{2} \sqrt{h^2 + k^2 + l^2} \operatorname{cosec} \theta \cot \theta \delta \theta$

and $\frac{\delta a}{a} = -\cot \theta \delta \theta.$

Systematic observational errors may arise in measuring the positions of lines on a film using the usual type of measuring instrument. An observer may systematically place the cross-hairs slightly to one side of the position of maximum line density, particularly if the background blackening has a marked slope. We have noticed that there is often a slight systematic discrepancy between readings made independently by the two of us.

In the thick specimens, absorption is the over-riding source of error, while in the specimen of "optimum" absorption and medium thickness, the effect of absorption is very slight. Hence the thick specimens give a linear plot against the absorption error function. When, however, the effect of absorption is negligible, the plot is no longer linear against this function; the only remaining source of error is observational and the plot becomes instead linear against $\cot\theta$. An intermediate case exists for the undiluted specimen of medium thickness. Here the plot is not strictly linear against either the absorption error function or against $\cot\theta$. The effect of observational errors being comparable with the absorption error, the plot is nearly linear against a mean of $\cot\theta$ and $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$.

Having considered the question of the overall linearity of the plots, it is necessary to investigate the consistency with which any given type of plot will lead to a single value for a . Large-scale plots of apparent a vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for the high-angle lines ($\theta > 30^\circ$) are shown in figures 5 *a* and 5 *b*.

In both cases, the extrapolations for the medium and thick specimens converge very nearly to a point in spite of the considerable difference in slope. The following table gives a list of the extrapolated a values obtained, the maximum extrapolation deviation in each case being ± 0.0001 kx.

Specimen	a from $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ extrapolation	Temp.
(a) Medium diluted	8.6863 kx.	15°.8
(b) Thick diluted	8.6861 kx.	15°.4
(c) Medium undiluted	8.6866 kx.	16°.2
(d) Thick undiluted	8.6864 kx.	16°.4

Mean value for $a = 8.6864 \pm 0.0003$ kx.

It will be noticed that the medium specimens in each case give a slightly larger value for a than the thick, and that the undiluted specimens give slightly higher values than the diluted. The slightly higher temperatures at which the undiluted specimens were photographed would tend to give slightly higher values for a . It is unlikely that the small difference of annealing temperature would have any measurable effect. Even so, the maximum error in the mean value of a from the four results is only about one part in 30,000. It is of interest that the value of a derived from the medium diluted specimen of "optimum" absorption is very close to the mean value.

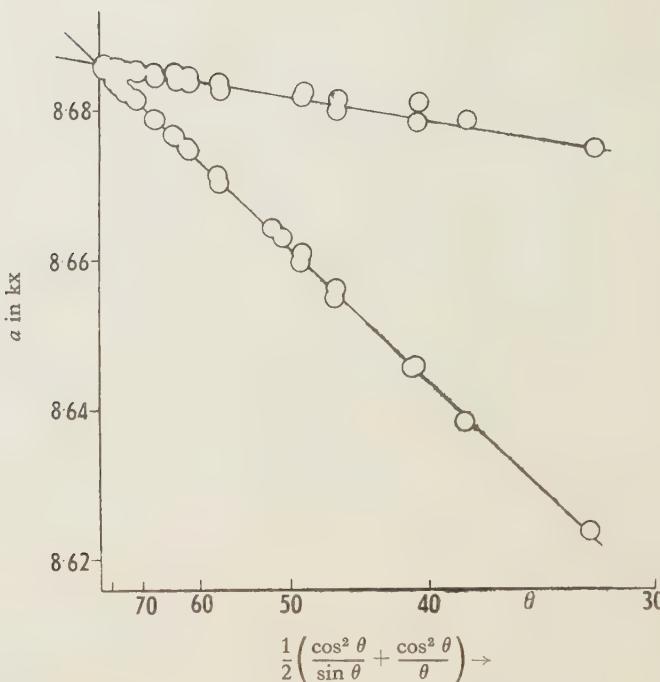


Figure 5 a. Medium thickness diluted specimen (upper plot).
Thick diluted specimen (lower plot).

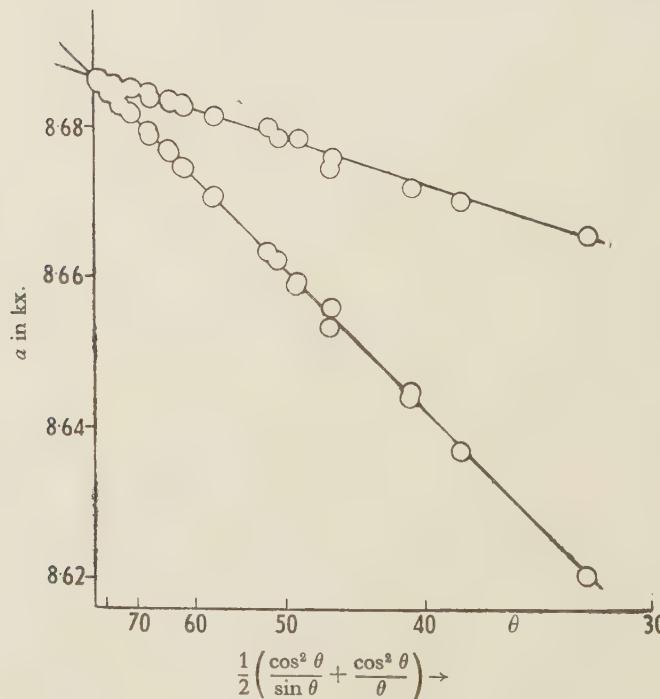


Figure 5 b. Medium thickness undiluted specimen (upper plot).
Thick undiluted specimen (lower plot).

Figure 5. Large-scale plots of α against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ for lines with $\theta > 30^\circ$.

A similar large-scale plot was made for specimen (*a*) (diluted, medium thickness) against the function which gave the best overall linearity, namely, $\cot \theta$. This is shown in figure 6.

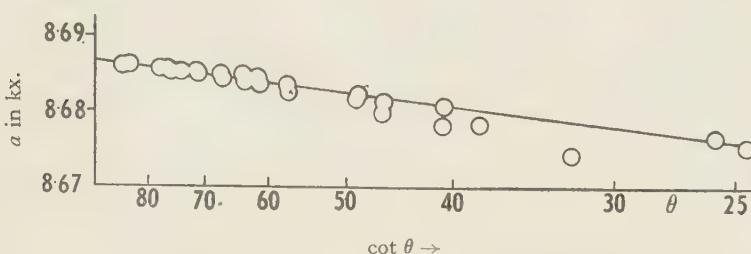


Figure 6. Medium thickness diluted specimen.
Large-scale plot of a against $\cot \theta$ for lines with $\theta > 25^\circ$.

The extrapolated value of a is 8.6867 kx., which is higher than that obtained above. It was noticed that the $\cot \theta$ plot tended to emphasize the effect of random errors in measurement, giving a slightly more "scattered" plot than the one against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$.

The enclosure of specimens in thin-walled silica or Lindemann-glass tubes does not appear to cause any new errors.

§ 5. EFFECT OF WRONG CAMERA ANGLE

The effect of an error in θ_k , the camera angle, is to cause a flexure in the plot of a vs. $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ at high angles. Figures 7 *a* and 7 *b* show this effect on data obtained from specimen (*b*). The a values used were calculated using θ_k in error by 0.1% in a positive and negative sense. A positive error in θ_k causes an upward flexure, and *vice versa*. The symmetry of the two effects confirms the accuracy of determination of the camera angle ($\theta = 86^\circ 693$) by Wilson and Lipson (1941).

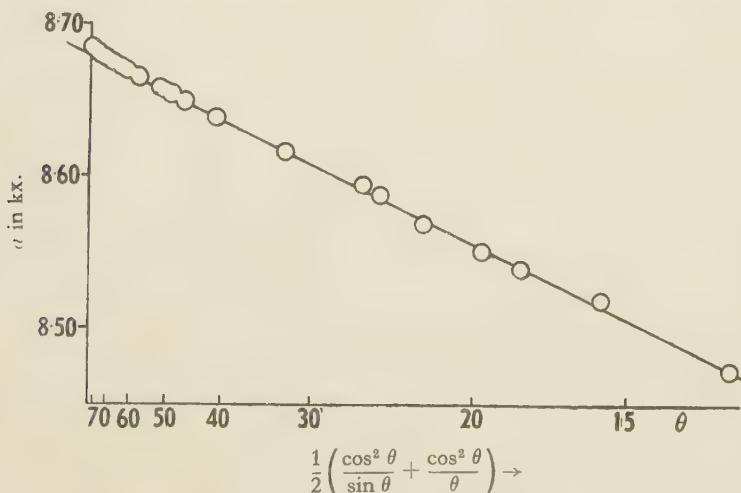
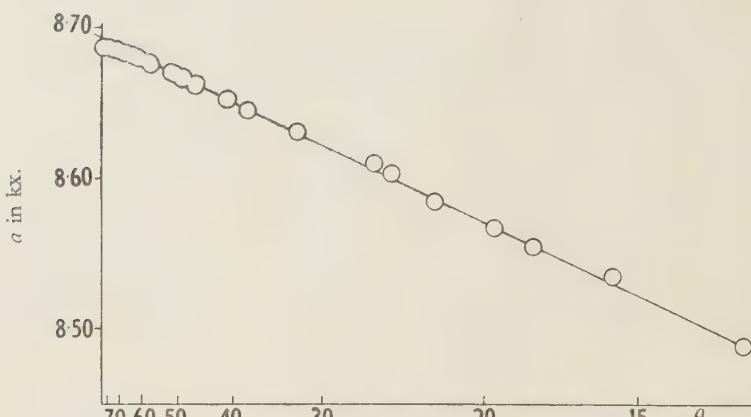


Figure 7 *a*. θ_k in error by +0.1 %.



$$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \rightarrow$$

Figure 7 b. θ_k in error by -0.1% .Figure 7. Effect of wrong camera angle, θ_k .Plots of a against $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ for thick diluted specimen.

These authors also discussed the source of error and showed that errors in a due to this cause are proportional to $\theta \cot \theta$. It is advisable to use a camera which can record lines with θ approaching 85° , otherwise the flexure in the plot may be unobservable and an unsuspected source of error be present.

§ 6. METHOD OF CALIBRATING CAMERA

The recommendation of Wilson and Lipson (1941) is to calibrate by direct measurement. Some cameras are so constructed, however, that this is impossible, and θ_k must then be derived from the high-angle lines on a quartz photograph. The basis of the method as described by Bradley and Jay (1933) is to derive values of θ_k from each high-order reflection and then to use an extrapolation technique. These authors showed that,

if $\frac{\delta a}{a} \propto \cos^2 \theta$,

then $\frac{\delta \theta_k}{\theta_k} \propto \frac{\sin 2\theta}{2\theta}$.

Hence the true value of θ_k is found by plotting the apparent values against $\frac{\sin 2\theta}{2\theta}$ and extrapolating linearly to zero (corresponding to $\theta = 90^\circ$).

We have shown that with well-constructed cameras absorption is the main source of error, and that

$$\frac{\delta a}{a} \propto \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$$

In this case it is easily proved that

$$\frac{\delta \theta_k}{\theta_k} \propto \frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta} \right).$$

Hence a plot of θ_k against $\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$ should give a straight line, and extrapolation to zero value of this function (corresponding to $\theta = 90^\circ$) should give the correct value of θ_k . Table 2 gives the values of $\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$ for the angles of reflection for quartz recommended by Wilson and Lipson (1941).

We have tried out this method of extrapolation on the results of Wilson and Lipson for films 873, 876, 877, which were all taken with the camera we used. The values derived for θ_k were $86^\circ 687$, $86^\circ 694$, $86^\circ 704$; mean $\theta_k = 86^\circ 695$,

Table 2

Values of $\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$ for quartz. Cu radiation, 18° c.

Line	θ ($^\circ$)	$\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$	Line	θ ($^\circ$)	$\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$
412 a_1	61.304	0.817	502 a_1	71.632	0.443
412 a_2	61.567	0.806	225 a_1		
305 a_1	63.631	0.723	502 a_2		
305 a_2	63.920	0.711	225 a_2	72.065	0.430
116 a_1	65.613	0.647	331 a_1		
116 a_2	65.931	0.636	331 a_2	72.509	0.417
501 a_1			420 a_1	73.319	0.392
501 a_2	very faint		420 a_2	73.803*	0.378
404 a_1			315 a_1	75.092*	0.341
404 a_2			315 a_2		
206 a_1	68.217	0.555	421 a_1	75.606	0.327
206 a_2	68.578	0.542	421 a_2		
			234 a_1	76.138	0.312
413 a_1	68.951	0.530	234 a_2	76.772	0.295
413 a_2	69.326	0.517	216 a_1	77.394	0.278
330 a_1	70.162	0.490	216 a_2	78.552	0.248
330 a_2	70.562	0.477	216 a_2	79.280	0.230

* These angles are given erroneously in table 4 of Wilson and Lipson's paper (1941), owing to a proof error.

mean deviation = $0^\circ 006$. The above authors, using a $\frac{\sin 2\theta}{2\theta}$ plot, had obtained $86^\circ 688$, $86^\circ 697$, $86^\circ 709$; mean $\theta_k = 86^\circ 698$, mean deviation = $0^\circ 007$. The camera angle derived by direct measurement is $86^\circ 693$, which is taken as the correct value. It will therefore be seen that the $\frac{\cos \theta}{\theta} \left(1 + \frac{\sin \theta}{\theta}\right)$ plot gives a more accurate result for θ_k in this case.

We should like to emphasize the recommendations of Wilson and Lipson that cameras should be calibrated by direct measurement wherever possible. When quartz has to be used, we would advise that at least three photographs be taken.

§ 7. RECOMMENDATIONS ON PROCEDURE

It is obvious that if a number of factors are contributing to the error, each of the factors having a different dependence on θ , no satisfactory linear plot of a vs. $f(\theta)$ can in general be obtained. The eccentricity error can, however, be almost entirely avoided by using a well-made camera, which should be a *sine qua non* in an investigation claiming the highest accuracy. The principal remaining source of error is then due to absorption, and linear extrapolation over a wide range becomes possible. It may not always be easy to assess the importance of eccentricity in the camera being used. In such cases it is advisable to calibrate the camera for extrapolation, following a procedure similar to that described in this paper. That is to say, the extrapolation function best suited to the particular camera should be derived empirically.

The first general recommendation, then, is to minimize the possible sources of error by using a well-designed and accurately constructed camera. Secondly, whether the Bradley-Jay or van Arkel arrangement is used, the method of film measurement using a camera angle described by Bradley and Jay (1932) and by Lipson and Wilson (1941) should be employed as it avoids uniform film-shrinkage errors. It is necessary, however, to know the camera angle accurately. We have shown in this paper that the effect of 0·1% error in the camera angle is easily noticed in an extrapolation, and Wilson and Lipson observed it with an error of only 0·06%. Hence the linearity of the plot at very high angles should provide another check on the accuracy of calibration of the camera. Thirdly, care should be taken to avoid "hot spots" on the target and to use an effectively circular focal spot.

Four conditions need to be considered in deciding on an extrapolation procedure :

- (a) It should give a consistent value for a whatever the nature of the specimen.
- (b) The low-angle limit of linearity of the plot should be as low as possible.
- (c) The compression of the high-angle points towards the extrapolation limit should be considerable.
- (d) The slope of the extrapolation should be as small as possible.

It is clear from the above results that a thick absorbing specimen gives an accurate linear plot of a vs. $\frac{1}{2}\left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}\right)$ down to the lowest recorded values of θ .

This advantage is somewhat outweighed by the greatly increased slope of the extrapolation. A thinner specimen of "optimum" absorption will, on the other hand, give rise to a very small extrapolation slope. The plot in general will not be linear over the whole range, but a plot of a vs. $\frac{1}{2}\left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}\right)$ will be accurately linear down to an angle of *about* 30° . This is a very much lower limit than is possible with a plot against $\cos^2 \theta$. Although a plot against $\cot \theta$ for such a specimen *may* have a greater range of linearity, it has the disadvantage that the high-angle points are not brought very close to the extrapolation limit. It also tends to accentuate the effect of random errors. Further, it has been

demonstrated for such a specimen that the plot against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ gives a value for a very close to the mean obtained from a number of specimens.

In order to obtain highest accuracy it is therefore recommended:

- (a) To make a thin specimen of "optimum" absorption.
- (b) To choose x radiation of the right wave-length to give high-angle lines; in particular, to ensure that at least one line has $\theta > 80^\circ$. The closer this final line is to $\theta = 90^\circ$, the greater the accuracy, no matter what extrapolation method is used.
- (c) To plot apparent a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ and to extrapolate linearly to zero value of this function. Lines with θ values as low as 30° can be included in the plot. This means that a far greater number of lines than usually considered can justifiably be used, giving the extrapolation greater certainty.

In critical cases it may be advisable to make a number of specimens of different thickness and absorption and to take the mean value of the results.

It must be emphasized that these recommendations have effect only when the eccentricity error is negligible, and we have urged that cameras be so designed and constructed that this is so. If, however, the effect of eccentricity is very much greater than that of absorption, a plot against $\cos^2\theta$ would be more correct. It is our experience that this is rarely the case, i.e. that absorption is usually the more important source of error.

If the problem is such that a reasonably accurate value of the cell dimension has to be derived from a few low-angle lines only, it would be preferable to make a thick absorbing specimen and again to use the $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ plot. The reason for this is that the extrapolation will have greater certainty than would be the case for the low-angle lines of a thin specimen. At the same time, it should be borne in mind that a thick specimen causes a considerable diminution in intensity of low-angle lines.

Our recommendations may be criticized on the grounds that they are based on the examination of one substance only, Cu_9Al_4 . There is, however, no reason for supposing any uniqueness of behaviour for this substance in the derivation of accurate unit-cell dimensions. Also, the different types of specimens prepared were chosen so as to give a considerable variation in properties.

A table of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ calculated for every tenth of a degree is appended (table 3). The calculations in this paper were carried out on a Marchant electric calculating machine with automatic division.

ACKNOWLEDGMENTS

We are indebted to Dr. A. J. Bradley, F.R.S., for the sample of Cu_9Al_4 used, and to Drs. H. Lipson and A. J. C. Wilson for several helpful discussions. The work was done in connection with an investigation on graphite carried out for the British Coal Utilisation Research Association.

Table 3

Table of $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$

θ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
10°	5·572	5·513	5·456	5·400	5·345	5·291	5·237	5·185	5·134	5·084
11	5·034	4·986	4·939	4·892	4·846	4·800	4·756	4·712	4·669	4·627
12	4·585	4·544	4·504	4·464	4·425	4·386	4·348	4·311	4·274	4·238
13	4·202	4·167	4·133	4·098	4·065	4·032	3·999	3·967	3·935	3·903
14	3·872	3·842	3·812	3·782	3·753	3·724	3·695	3·667	3·639	3·612
15	3·584	3·558	3·531	3·505	3·479	3·454	3·429	3·404	3·379	3·355
16	3·331	3·307	3·284	3·260	3·237	3·215	3·192	3·170	3·148	3·127
17	3·105	3·084	3·063	3·042	3·022	3·001	2·981	2·962	2·942	2·922
18	2·903	2·884	2·865	2·847	2·828	2·810	2·792	2·774	2·756	2·738
19	2·921	2·704	2·687	2·670	2·653	2·636	2·620	2·604	2·588	2·572
20	2·556	2·540	2·525	2·509	2·494	2·479	2·464	2·449	2·434	2·420
21	2·405	2·391	2·376	2·362	2·348	2·335	2·321	2·307	2·294	2·280
22	2·267	2·254	2·241	2·228	2·215	2·202	2·189	2·177	2·164	2·152
23	2·140	2·128	2·116	2·104	2·092	2·080	2·068	2·056	2·045	2·034
24	2·022	2·011	2·000	1·989	1·978	1·967	1·956	1·945	1·934	1·924
25	1·913	1·903	1·892	1·882	1·872	1·861	1·851	1·841	1·831	1·821
26	1·812	1·802	1·792	1·782	1·773	1·763	1·754	1·745	1·735	1·726
27	1·717	1·708	1·699	1·690	1·681	1·672	1·663	1·654	1·645	1·637
28	1·628	1·619	1·611	1·602	1·594	1·586	1·577	1·569	1·561	1·553
29	1·545	1·537	1·529	1·521	1·513	1·505	1·497	1·489	1·482	1·474
30	1·466	1·459	1·451	1·444	1·436	1·429	1·421	1·414	1·407	1·400
31	1·392	1·385	1·378	1·371	1·364	1·357	1·350	1·343	1·336	1·329
32	1·323	1·316	1·309	1·302	1·296	1·289	1·282	1·276	1·269	1·263
33	1·256	1·250	1·244	1·237	1·231	1·225	1·218	1·212	1·206	1·200
34	1·194	1·188	1·182	1·176	1·170	1·164	1·158	1·152	1·146	1·140
35	1·134	1·128	1·123	1·117	1·111	1·106	1·100	1·094	1·098	1·083
36	1·078	1·072	1·067	1·061	1·056	1·050	1·045	1·040	1·034	1·029
37	1·024	1·019	1·013	1·008	1·003	0·998	0·993	0·988	0·982	0·977
38	0·972	0·967	0·962	0·958	0·953	0·948	0·943	0·938	0·933	0·928
39	0·924	0·919	0·914	0·909	0·905	0·900	0·895	0·891	0·886	0·881
40	0·877	0·872	0·868	0·863	0·859	0·854	0·850	0·845	0·841	0·837
41	0·832	0·828	0·823	0·819	0·815	0·810	0·806	0·802	0·798	0·794
42	0·789	0·785	0·781	0·777	0·773	0·769	0·765	0·761	0·757	0·753
43	0·749	0·745	0·741	0·737	0·733	0·729	0·725	0·721	0·717	0·713
44	0·709	0·706	0·702	0·698	0·694	0·690	0·687	0·683	0·679	0·676
45	0·672	0·668	0·665	0·661	0·657	0·654	0·650	0·647	0·643	0·640
46	0·636	0·632	0·629	0·625	0·622	0·619	0·615	0·612	0·608	0·605
47	0·602	0·598	0·595	0·591	0·588	0·585	0·582	0·578	0·575	0·572
48	0·569	0·565	0·562	0·559	0·556	0·553	0·549	0·546	0·543	0·540
49	0·537	0·534	0·531	0·528	0·525	0·522	0·518	0·515	0·512	0·509
50	0·506	0·504	0·501	0·498	0·495	0·492	0·489	0·486	0·483	0·480
51	0·477	0·474	0·472	0·469	0·466	0·463	0·460	0·458	0·455	0·452
52	0·449	0·447	0·444	0·441	0·439	0·436	0·433	0·430	0·428	0·425
53	0·423	0·420	0·417	0·415	0·412	0·410	0·407	0·404	0·402	0·399
54	0·397	0·394	0·392	0·389	0·387	0·384	0·382	0·379	0·377	0·375

Table 3 (continued)

θ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
55	0·372	0·370	0·367	0·365	0·363	0·360	0·358	0·356	0·353	0·351
56	0·349	0·346	0·344	0·342	0·339	0·337	0·335	0·333	0·330	0·328
57	0·326	0·324	0·322	0·319	0·317	0·315	0·313	0·311	0·309	0·306
58	0·304	0·302	0·300	0·298	0·296	0·294	0·292	0·290	0·288	0·286
59	0·284	0·282	0·280	0·278	0·276	0·274	0·272	0·270	0·268	0·266
60	0·264	0·262	0·260	0·258	0·256	0·254	0·252	0·250	0·249	0·247
61	0·245	0·243	0·241	0·239	0·237	0·236	0·234	0·232	0·230	0·229
62	0·227	0·225	0·223	0·221	0·220	0·218	0·216	0·215	0·213	0·211
63	0·209	0·208	0·206	0·204	0·203	0·201	0·199	0·198	0·196	0·195
64	0·193	0·191	0·190	0·188	0·187	0·185	0·184	0·182	0·180	0·179
65	0·177	0·176	0·174	0·173	0·171	0·170	0·168	0·167	0·165	0·164
66	0·162	0·161	0·160	0·158	0·157	0·155	0·154	0·152	0·151	0·150
67	0·148	0·147	0·146	0·144	0·143	0·141	0·140	0·139	0·138	0·136
68	0·135	0·134	0·132	0·131	0·130	0·128	0·127	0·126	0·125	0·123
69	0·122	0·121	0·120	0·119	0·117	0·116	0·115	0·114	0·112	0·111
70	0·110	0·109	0·108	0·107	0·106	0·104	0·103	0·102	0·101	0·100
71	0·099	0·098	0·097	0·096	0·095	0·094	0·092	0·091	0·090	0·089
72	0·088	0·087	0·086	0·085	0·084	0·083	0·082	0·081	0·080	0·079
73	0·078	0·077	0·076	0·075	0·075	0·074	0·073	0·072	0·071	0·070
74	0·069	0·068	0·067	0·066	0·065	0·065	0·064	0·063	0·062	0·061
75	0·060	0·059	0·059	0·058	0·057	0·056	0·055	0·055	0·054	0·053
76	0·052	0·052	0·051	0·050	0·049	0·048	0·048	0·047	0·046	0·045
77	0·045	0·044	0·043	0·043	0·042	0·041	0·041	0·040	0·039	0·039
78	0·038	0·037	0·037	0·036	0·035	0·035	0·034	0·034	0·033	0·032
79	0·032	0·031	0·031	0·030	0·029	0·029	0·028	0·028	0·027	0·027
80	0·026	0·026	0·025	0·025	0·024	0·023	0·023	0·023	0·022	0·022
81	0·021	0·021	0·020	0·020	0·019	0·019	0·018	0·018	0·017	0·017
82	0·017	0·017	0·016	0·015	0·015	0·015	0·014	0·014	0·013	0·013
83	0·013	0·012	0·012	0·012	0·011	0·011	0·010	0·010	0·010	0·010
84	0·009	0·009	0·009	0·008	0·008	0·008	0·007	0·007	0·007	0·007
85	0·006	0·006	0·006	0·006	0·005	0·005	0·005	0·005	0·005	0·004
86	0·004	0·004	0·004	0·003	0·003	0·003	0·003	0·003	0·003	0·002
87	0·002	0·002	0·002	0·002	0·002	0·002	0·001	0·001	0·001	0·001
88	0·001	0·001	0·001	0·001	0·001	0·001	0·001	0·000	0·000	0·000

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WALL- AND SALT-ABSORPTION CORRECTIONS IN RADIUM-CONTENT MEASUREMENTS

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ABSTRACT. The measurement of radium content by the gamma-ray method involves corrections for the absorption of the radiation in the wall of the container and in the radioactive material itself. Corrections for cylindrical containers constructed of platinum-iridium, gold, a gold-silver alloy and monel metal have been determined experimentally for wall thicknesses up to 2 mm. and external diameters up to 8 mm., using radium cells and absorbing tubes to simulate radium containers. Measurements of the absorption in powdered materials are described and an empirical formula representing the absorption both for the powdered materials and the metal tubes is deduced. The results provide an experimental basis for the estimation of the absorption in radium salts, and examples of their application to practical cases are given.

§ 1. INTRODUCTION

THE determination of the radium content of a radium container involves an important correction for the absorption of the gamma rays in the wall of the container and, in the case of certain containers, a correction for the absorption in the radium salt itself. Owen and Naylor (1922) calculated the wall-absorption corrections for platinum, silver and glass containers respectively, using a formula which involves the absorption coefficient of the gamma rays in the material of the container. The corrections for platinum and monel metal were determined experimentally at the National Physical Laboratory by Kaye, Aston and the writer in 1934, nests of absorbing tubes being used as a convenient means of simulating cylindrical radium containers. The measurements covered a range of wall thicknesses from 0·3 to 1·5 mm. and a range of external diameters from 1·5 to 8 mm. It later proved necessary to extend the measurements to wall thicknesses of 2 mm., and the opportunity was therefore taken to repeat the earlier measurements, particularly as radium cells and absorbing tubes became available which were more suitable in several respects than those used previously. These measurements are dealt with in the earlier part of this paper, while the later part deals with measurements undertaken to obtain data on which to base the estimation of the correction for the absorption in the radium salt itself.

§ 2. ABSORPTION IN CYLINDRICAL METAL TUBES

2.1. *Radium sources and absorbing tubes.** The metals for which absorption measurements have been made are : (a) Platinum-iridium (90% Pt, 10% Ir),

* We are indebted to Messrs. Eldorado Gold Mines, Ltd., for the loan of the radium and to Messrs. Johnson, Matthey and Co., Ltd., for the construction and loan of the absorbing tubes used in the measurements.

which will be referred to as platinum; (b) gold; (c) an alloy of gold (67%), silver (20·65%), copper (10·9%) and platinum (1·45%), which will be referred to as gold-silver alloy; (d) monel metal (67% Ni, 28% Cu, 5% Fe, Mn, etc.).

Three radium cells were obtained for the measurements. Each consisted of radium salt enclosed in a cylindrical monel-metal cell, the radium contents being approximately 8, 20 and 20 mg. radium element respectively. The wall thickness of each cell was 0·1 mm., the external length 25 mm. and the external diameters 0·8, 2·0 and 4·0 mm. The cells were closed by solid plugs of monel metal 5 mm. long, so that manipulation with forceps could be carried out without risk of damaging the thin walls. Contact photographs showed that the radium was distributed uniformly throughout the internal length of the cell.

Each radium cell was provided with five closely-fitting platinum absorbing tubes of length 35 mm. and wall thicknesses approximately 0·3, 0·5, 1·0, 1·5 and 2 mm. respectively, i.e. there were in all fifteen platinum tubes. The external diameters of the tubes ranged from 1·4 to 4·8 mm. for the small diameter cell, from 2·6 to 6·0 mm. for the medium diameter cell, and from 4·6 to 8·0 mm. for the largest diameter cell. Two gold tubes of wall thicknesses approximately 1 and 2 mm. were available for each radium cell. In the case of monel metal and the gold-silver alloy, five tubes were made for use with the smallest diameter cell, the wall thicknesses ranging from 0·3 to 2 mm.

2.2. Measurement of wall thicknesses of absorbing tubes.* The wall thicknesses of the platinum and the gold-silver alloy tubes were determined (1) by measuring the external and internal diameters at the ends with a precision microscope; (2) by calculating the internal diameters, using the known mass, density and external dimensions; (3) by measuring the external diameters with a micrometer screw gauge and the internal diameters by inserting cylinders of known diameters. Method (3) was omitted in the case of the gold and the monel-metal tubes. In general, method (1) gave the smallest values, the results indicating that the walls of the tubes were, on the average, 0·02 mm. thinner at the ends than elsewhere. The values obtained by method (2) were generally intermediate between those by methods (1) and (3), and were accordingly adopted as being the best values of the average wall thicknesses. Incidentally, the density of the platinum-iridium was found by the Metrology Division of the Laboratory to be 21·53, that of the gold 19·21, gold-silver alloy 14·79, and monel metal 8·82₅, the estimated accuracy being ± 1 part in 1000.

2.3. Absorption measurements. The apparatus used for the absorption measurements consisted of the combined ionization chamber and electroscope (Perry, 1936) used in radium-content tests at the National Physical Laboratory, the thickness of the lead filter on the front of the chamber being 0·5 cm. The measurements consisted of comparing the ionization I_0 produced by a radium cell with the ionization I when the cell was enclosed in a metal absorbing tube, the radium being supported in a wooden stand parallel to the front face of the ionization chamber. The "measured" percentage absorption correction c_m is

* The co-operation of the Metrology Division of the Laboratory is gratefully acknowledged in connection with these measurements.

then given by $c_m = 100 \left(\frac{I_0 - I}{I} \right)$. The absorption corrections were, within the limits of experimental error, independent of the distance between the radium and the chamber for distances normally used, viz., 30 to 120 cm. The majority of the measurements were made at distances between 30 and 60 cm., as these gave convenient ionization currents.

§ 3. RESULTS OF ABSORPTION MEASUREMENTS

3.1. *Wall-absorption corrections.* The results of the measurements of the absorption in metal tubes are given in table 1, columns (1) and (2) of which give the external diameters and wall thicknesses, and column (3) the "measured" corrections. As explained in the 1936 paper, owing to the presence of the wall of the radium cell, the measured correction is slightly less than it would be were the absorbing tube completely filled with radium, and an allowance for this has to be made. This allowance was made by multiplying the measured correction c_m by the ratio c_1/c_2 , where c_1 and c_2 are respectively the calculated corrections for the tube completely filled with radium and for the same tube when the cell wall is interposed between the inside of the tube and the radium. An accurate value of the absorption coefficient of the gamma rays in the material of the tube is not necessary for this correction factor, and the values used in the calculations were approximate estimations based on preliminary measurements. The "true" corrections, i.e. the values in column 3 corrected for the presence of the cell wall, are given in column 4.

Table 2 contains the derived values of the corrections for tubes of normal dimensions. In the case of platinum, gold and monel metal, the majority of these values have been obtained by graphical interpolation of the results given in table 1. Graphical extrapolation was necessary to derive the corrections for the thinner-walled tubes of large diameter, but for such tubes the variation of the correction with the external diameter is small, and extrapolation introduces no appreciable uncertainty. In the case of gold-silver alloy, for which the measurements were limited to tubes having diameters between 1·4 and 5 mm., Owen and Naylor's formula (1922) was used as a means of extrapolating the results to obtain the corrections for tubes of larger diameter.

3.2. *Discussion of results.* The values of the corrections given in table 2 represent the percentage by which the observed radium content has to be increased in order to obtain the true content. They are considered to be reliable to within $\pm 0\cdot3$ for the thicker tubes and to within less than this figure for the thinner tubes. It should be noted that the values are only applicable when the measuring apparatus is similar to that used at the National Physical Laboratory, and that modifications in the apparatus, e.g., a change in the lead filter or in the lining of the ionization chamber, introduce variations in the corrections. A slight increase in the corrections is necessary when the distance of the radium from the chamber is less than 30 cm. The increase in the percentage correction in the case of platinum and gold is about 0·1 per mm. of wall thickness when the distance is 20 cm., and 0·05 per mm. of wall thickness when the distance is 25 cm. Incidentally, a change of 0·1 in the absorption

Table 1. Experimental wall-absorption corrections. (Wall thickness of monel-metal radium cells 0.1 mm.; lead filter 0.5 cm. thick.)

External diameter of absorbing tube (mm.)	Wall thickness of absorbing tube (mm.)	Percentage absorption correction	
		As measured	Corrected for presence of cell wall
<i>Platinum</i>			
1.39 ₇	0.27 ₀	3.0	3.3
1.77 ₈	0.46 ₀	5.5	5.7
2.80 ₉	0.98 ₀	12.2	12.6
3.78 ₇	1.46 ₅	18.5	18.9
4.81 ₃	1.95 ₀	25.0	25.4
2.65 ₀	0.29 ₅	3.8	4.0
3.01 ₅	0.48 ₀	6.1	6.3
4.01 ₃	0.97 ₀	12.7	13.1
5.00 ₉	1.47 ₅	19.4	19.9
6.01 ₀	1.96 ₀	26.1	26.6
4.65 ₆	0.29 ₀	3.6	3.8
4.98 ₆	0.46 ₀	6.2	6.4
5.97 ₇	0.94 ₅	13.1	13.5
7.00 ₃	1.44 ₅	19.9	20.4
7.98 ₇	1.95 ₅	27.3	27.8
<i>Gold</i>			
2.79 ₉	0.94 ₅	10.6	10.9
4.80 ₀	1.93 ₀	22.7	23.1
3.98 ₉	0.96 ₀	11.5	11.9
5.99 ₉	1.95 ₀	23.5	23.9
5.99 ₃	0.94 ₀	11.6	11.9
7.99 ₃	1.94 ₀	24.5	24.9
<i>Gold-silver alloy</i>			
1.45 ₅	0.29 ₅	2.0	2.1
1.85 ₇	0.49 ₅	3.4	3.6
2.83 ₈	0.97 ₅	7.3	7.5
3.84 ₆	1.47 ₅	11.2	11.4
4.90 ₇	2.00 ₀	15.4	15.7
<i>Monel metal</i>			
1.46 ₅	0.30 ₀	0.7	0.7
1.83 ₅	0.48 ₀	1.2	1.2
2.85 ₀	0.99 ₅	2.4	2.5
3.84 ₅	1.44 ₅	3.6	3.7
4.82 ₉	1.93 ₅	4.9	5.0
5.49*	0.33 ₂	0.8	0.8
6.08*	0.59 ₉	1.3	1.3
6.87*	0.97 ₆	2.7	2.9
7.91*	1.47 ₁	4.1	4.3

* Results obtained in a previous investigation (1936), using a glass radium cell of 0.35 mm. wall thickness and 4.6 mm. external diameter.

Table 2. Percentage wall-absorption corrections applicable to the measured radium contents of uniformly filled cylindrical tubes. Lead filter 0.5 cm. thick.

External diameter of tube (mm.)	Wall thickness of tube (mm.)									
	0.3	0.4	0.5	0.6	0.8	1.0	1.25	1.5	1.75	2.0
<i>Platinum tubes</i>										
1.5	3.7	4.8	5.9							
2.0	3.9	5.0	6.3	7.4						
2.5	4.0	5.2	6.5	7.7	10.1	12.5				
3.0	4.1	5.3	6.7	7.9	10.4	12.9	15.8			
3.5	4.2	5.5	6.8	8.1	10.7	13.2	16.2	19.0		
4.0	4.3	5.5	6.9	8.2	10.9	13.4	16.6	19.5	22.3	
5.0	4.3	5.7	7.1	8.4	11.1	13.8	17.1	20.2	23.3	26.3
6.0	4.4	5.7	7.2	8.6	11.3	14.0	17.5	20.8	24.0	27.0
7.0	4.4	5.8	7.2	8.7	11.4	14.2	17.8	21.2	24.6	27.7
8.0	4.4	5.8	7.3	8.8	11.5	14.3	18.0	21.6	25.1	28.4
<i>Gold tubes</i>										
1.5	3.4	4.5	5.4							
2.0	3.5	4.7	5.8	6.8						
2.5	3.6	4.8	6.0	7.1	9.2	11.2				
3.0	3.7	4.9	6.2	7.3	9.5	11.6	14.3			
3.5	3.8	5.0	6.2	7.5	9.8	12.0	14.7	17.4		
4.0	3.9	5.0	6.3	7.6	10.0	12.3	15.0	17.8	20.4	
5.0	3.9	5.1	6.4	7.6	10.1	12.7	15.5	18.4	21.2	24.0
6.0	4.0	5.1	6.5	7.6	10.2	12.9	15.8	18.8	21.7	24.7
7.0	4.0	5.1	6.5	7.7	10.2	12.9	16.0	19.1	22.2	25.2
8.0	4.0	5.1	6.5	7.7	10.3	13.0	16.1	19.4	22.6	25.7
<i>Gold-silver alloy tubes</i>										
1.5	2.2	2.8	3.5							
2.0	2.3	3.0	3.7	4.4						
2.5	2.4	3.1	3.8	4.6	6.1					
3.0	2.4	3.1	3.9	4.7	6.3	7.6	9.5			
4.0	2.5	3.2	4.0	4.8	6.3	7.9	9.7	11.7	13.4	
5.0	2.5	3.3	4.0	4.8	6.4	8.0	9.8	11.9	13.8	15.7
6.0	2.5	3.3	4.1	4.9	6.5	8.0	9.9	12.2	14.0	16.0
8.0	2.5	3.3	4.1	4.9	6.5	8.1	10.1	12.4	14.3	16.4
<i>Monel-metal tubes</i>										
1.5	0.7	1.0	1.2							
2.0	0.8	1.1	1.3	1.5						
3.0	0.8	1.1	1.3	1.6	2.1	2.6				
4.0	0.8	1.1	1.4	1.6	2.2	2.8	3.3	3.9	4.5	
5.0	0.8	1.1	1.4	1.6	2.2	2.9	3.4	4.1	4.7	5.2
6.0	0.9	1.1	1.4	1.6	2.2	2.9	3.6	4.2	4.8	5.5
8.0	0.9	1.1	1.4	1.6	2.3	3.0	3.7	4.4	5.0	5.8

correction results in a change of 1 part in 1000 in the derived radium-content value.

The measurements in platinum confirm the earlier observations for wall thicknesses up to 0·8 mm., the differences being not greater than 0·3. For wall thicknesses of 1 mm. and upwards, the new values are slightly less than the earlier values, the differences being less marked the greater the diameter. This discrepancy arises mainly from a slight lack of uniformity of one of the absorbing tubes used in the earlier investigation, in which the wall thicknesses were determined at the ends of the tubes only, by a vernier microscope. These agreed in general with the average values, as calculated from the density, to within 0·02 mm. The wall thickness at the ends of the outer tube of the small diameter "nest" was however 0·05 mm. less than the average thickness. When allowance is made for this, the earlier and present series of measurements agree within the limits of experimental error.

The absorption coefficient of the gamma rays in platinum derived from the results is $1\cdot14 \text{ cm}^{-1}$, i.e. slightly lower than the earlier value, $1\cdot16 \text{ cm}^{-1}$. The coefficients for gold, gold-silver alloy, and monel metal are $1\cdot05 \text{ cm}^{-1}$, $0\cdot70 \text{ cm}^{-1}$ and $0\cdot25 \text{ cm}^{-1}$ respectively, and the corresponding mass-absorption coefficients are 0·053 for platinum, 0·055 for gold, 0·047 for gold-silver alloy and 0·028 for monel metal. For a lead filter 0·5 cm. thick, these values for platinum and gold are a little greater and that of monel metal a little less than those indicated by the curves which Oddie (1939) obtained from measurements with radium-measuring equipment of somewhat different design.

Table 2 contains sufficient values for the interpolation of corrections for tubes having wall thicknesses between 0·3 and 2 mm. and external diameters between 1·5 and 8 mm. Also, plotting the absorption correction against the absorption coefficient for tubes of identical dimensions yields a series of curves by means of which the corrections for tubes of any material of known absorption coefficient may be obtained. As is shown later, the value of the coefficient can be estimated to an accuracy sufficient for most purposes by the empirical formula (2) in §4.3.

§ 4. SALT-ABSORPTION CORRECTIONS

Most of the radium containers used in medical practice contain only a few milligrammes of radioactive material, the absorption of the gamma rays in which is negligible. When, however, the quantity of radioactive salt is 20 mg. or more, an appreciable absorption occurs and a "salt-absorption" correction is then necessary. The correction can be calculated (Thirring and Schweidler, 1912; Schweidler, 1912; Paterson *et al.*, 1917; Dufton, 1926; Holuba, 1937; Franz and Weiss, 1940), provided the absorption coefficient of the gamma rays in the salt is known, and a number of investigations of radioactive materials have been made to obtain the information required (Paterson *et al.*, 1917; Owen and Fage, 1921; Behounek, 1934; Franz and Weiss, 1935; Curtis, 1939). Owing to the cost of radium and the experimental difficulties involved, it has not been possible to measure directly the absorption in a radium salt. Attempts have been made at the National Physical Laboratory to measure the absorption by placing a radium container of small dimensions behind a larger one, but these

attempts provided no reliable results because it was not possible to estimate accurately the appropriate wall-absorption correction. It has therefore been necessary to derive the required data indirectly from the results of measurements in which ordinary powdered materials were used as absorbers.

4.1. Absorption measurements in powdered materials. The experimental part of the investigation consisted of measurements of the absorption of the gamma rays in powdered materials the constituents of which ranged from carbon (at. no. = 6) to uranium (at. no. = 92). Measurements were first undertaken in which the powdered material was enclosed in a vessel having plane walls, the radium cell being placed outside the vessel and in contact with the side of the vessel remote from the ionization chamber. These measurements served to indicate the dependence of the absorption on the density and composition of the absorbing specimen, but in order to obtain conditions more nearly similar to those of radium-content determinations, further measurements were made in which the radium cell was surrounded by the absorbing material. Preliminary measurements with vessels having plane walls showed that the absorption under these conditions is slightly less than when the radium is outside the specimen. To approximate more closely to the required conditions it was decided to use cylindrical vessels to contain the powder, and to support the radium cell axially inside the cylinders. Two ebonite cylinders of different diameters were constructed for these measurements. They were of external length 25.5 mm., internal length 20 mm., external diameters 13.4 and 23 mm. and internal diameters 11.3 and 20.4 mm. respectively. The 2-mm. diameter radium cell referred to in § 2.1 was used, and with this cell in position the internal volumes of the cylinders were 1.91 and 6.56 c.c., the absorbing thicknesses of powder when the cylinders were full being 4.65 mm. and 9.20 mm. Each material was finely powdered in an agate mortar before being transferred to the cylinder, and its apparent density was determined from the weight of the powder required to fill the cylinder.

The absorption in a powder was measured by comparing the ionization I_0 when the radium cell was enclosed in the otherwise empty cylinder with the ionization I when the cylinder was full. In deriving the absorption coefficient μ of the gamma rays in the powder from the ratio I/I_0 , account was taken of the curvature of the walls of the radium cell and the cylinder and of the presence of the wall of the radium cell. Assuming a parallel beam of gamma rays, it can be shown that

$$\frac{I}{I_0} = \frac{4}{\pi} \int_0^{\pi/2} \cos^2 \phi \, e^{-\mu \tau [(b^2 - a_1^2 \sin^2 \phi)^{1/2} - (a^2 - a_1^2 \sin^2 \phi)^{1/2}]} d\phi, \quad \dots \dots \dots (1)$$

where a_1 and a are the internal and external radii of the radium source and b is the internal radius of the cylinder containing the powder. Graphs were drawn for each cylinder showing the variation of I/I_0 with μ for values of μ up to 0.3 cm.^{-1} , and these graphs were used to obtain the values of μ corresponding to the experimental values of I/I_0 .

4.2. Experimental results. The mean results of the measurements are given in table 3, column 1 of which gives the composition of the material, column 2

the apparent density (g./c.c.), and columns 3 and 4 the measured linear and mass-absorption coefficients μ (cm.⁻¹) and μ/ρ (cm² g.⁻¹) respectively. The figures in column 5 are referred to later. The accuracy of the values of μ/ρ in column 4 is about $\pm 5\%$, and within these limits μ/ρ was the same for each cylinder, indicating that the absorption coefficient is practically independent of the radial thickness of the absorbing specimen for thicknesses between 0.5 and 1 cm. and of the internal diameter of the containing vessel for diameters between 1 and 2 cm. It is seen that materials containing only elements of low atomic number, i.e. less than that of barium (at. no.=56), have approximately the same mass absorption coefficient, the mean value for these materials being 0.031.

Table 3. Absorption in powdered materials. Radium source on axis of cylindrical vessel containing absorbing powder. Lead filter 0.5 cm. thick.

Absorbing material	Density of absorbing material	Measured linear and mass-absorption coefficient		μ/ρ based on empirical formula $\mu_e = 1.04 \times 10^{-25} + 2.5 \times 10^{-31} Z^3$
		μ	μ/ρ	
U ₃ O ₈	(g./c.c.) 3.95	(cm. ⁻¹) 0.255	(cm ² g. ⁻¹) 0.065	(cm ² g. ⁻¹) 0.065
Th(SO ₄) ₂ · 9H ₂ O	1.37	0.064	0.047	0.047
Bi ₂ (SO ₄) ₃	1.70	0.075	0.044	0.048
PbO	3.92	0.220	0.056	0.056
BaSO ₄	3.05	0.100	0.033	0.034
ZnS	2.42	0.072	0.030	0.031
S	1.31	0.040	0.031	0.032
MgO	0.473	0.015	0.032	0.031
C	0.91	0.029	0.032	0.031
<i>Metal tubes</i>				
Au	19.21	1.05	0.055	0.055
Pt/Ir	21.53	1.14	0.053	0.054
Gold-silver alloy	14.79	0.70	0.047	0.048
Monel metal	8.82 ₅	0.25	0.028	0.031

There is, however, a wide range of mass absorption coefficients in the case of those materials containing elements of high atomic number. We have included in table 3 the results of the measurements of the absorption in cylindrical metal tubes referred to in § 3.2. It will be noted that the mass-absorption coefficient of monel metal, which is representative of elements of low atomic number, is only slightly less than that of the corresponding powdered materials, while the mass-absorption coefficients of the other metals are intermediate between those of powdered materials containing elements of high atomic number.

4.3. *Derivation of the absorption coefficients of radium salts.* In order to derive the absorption coefficients of radium salts corresponding to the results given in table 3, it was found convenient to deal in terms of the absorption

coefficient per electron of each element, $\mu_e = \frac{A}{NZ} \cdot \frac{\mu}{\rho}$, where A and Z are the

atomic weight and atomic number and N is Avogadro's number (6.06×10^{23}). The absorption was considered to consist of two parts, one due to scattering and the other to photo-electric and other processes. It is known that the absorption in light elements is due almost entirely to scattering, the absorption per electron being practically independent of the atomic number. The results in table 3 are in agreement with this, the values of μ_e for these materials being from 0.99×10^{-25} to 1.06×10^{-25} . The contribution of the elements of high atomic number to the total absorption in a material was obtained by first deriving the absorption per molecule $\left(\frac{M}{N} \cdot \frac{\mu}{\rho}\right)$, where M is the molecular weight), and subtracting from this the absorption due to the elements of low atomic number, taking μ_e for the latter to be 1.04×10^{-25} . The values of μ_e for the elements of high atomic number so obtained were plotted against the atomic number, and it was found that both for powdered materials and metal tubes the points lay close to the curve* represented by

$$\mu_e = 1.04 \times 10^{-25} + 2.5 \times 10^{-31} Z^3. \quad \dots \dots (2)$$

The mass-absorption coefficients of the materials used in the measurements based on this expression are given in the final column of table 3, and the corresponding mass-absorption coefficients of the most commonly used radium salts are given in table 4.

Table 4. Mass-absorption coefficients of radium salts. Lead filter 0.5 cm. thick. Empirical basis $\mu_e = 1.04 \times 10^{-25} + 2.5 \times 10^{-31} Z^3$.

Radium salt	Mass absorption coefficient μ/ρ (cm. ² .g. ⁻¹)
RaSO ₄	0.055
RaBr ₂	0.051
RaCl ₂	0.057
RaCO ₃	0.058

§ 5. THEORETICAL SALT-ABSORPTION CORRECTIONS

5.1. *Completely filled container.* When a cylindrical container full of radium salt is situated symmetrically on the axis of the ionization chamber, the axis of the container being perpendicular to that of the chamber, then, assuming a parallel beam of gamma rays, the ratio of the measured ionization I to the ionization I_0 had there been no absorption in the radium salt is given by

$$\frac{I}{I_0} = 1 - \frac{8}{6\pi} (\mu d) + \frac{1}{8} (\mu d)^2 - \frac{4}{45\pi} (\mu d)^3, \quad \dots \dots (3)$$

where d is the internal diameter of the container and μ is the absorption coefficient of the gamma rays in the radium salt (Paterson *et al.*, 1917).

The values of the percentage absorption correction $100 \left(\frac{I_0 - I}{I} \right)$ calculated

* See Rutherford *et al.*, 1930; Kohlrausch, 1928; and Gray, 1931.

by means of (3) for values of μd up to 0.20 are given in table 5. It is seen that the percentage correction is approximately equal to $43\mu d$.

Table 5. Theoretical salt-absorption corrections (%).

μd	0.01	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20
Percentage absorption correction	0.4	0.9	1.7	2.6	3.4	4.3	5.2	6.0	6.9	7.8	8.7

5.2. *Partially filled container.* Franz and Weiss (1940) have shown that when a cylindrical container is only partially filled with radioactive material the absorption in the material is given by

$$\frac{I}{I_0} = 1 - a(\mu d) + b(\mu d)^2, \quad \dots\dots \quad (4)$$

in which the values of a and b depend on the ratio h/d , h being the depth of the radium salt when the axis of the container is horizontal. The ratio of the correction for a partially filled container to that for a completely filled container is nearly independent of μd for values of μd up to 0.2. Values of the ratio for different values of h/d are given in table 6. It is seen that the correction for a container less than half full is smaller than that for a full container, while the correction for a container more than half but not completely full slightly exceeds that for a full container. The formula (4) is based on the assumption that radon remains occluded in the radioactive material, which is true in the case of a number of radium salts, e.g. radium sulphate, crystalline radium chloride and radium bromide.

Table 6. Ratio of salt-absorption corrections for full and partially full containers

h/d	0.15	0.25	0.5	0.75	0.85	1.0
" Partially filled " correction	0.64	0.8	1.0	1.03	1.04	1.0
" Completely filled " correction						

§ 6. PRACTICAL SALT-ABSORPTION CORRECTIONS

6.1. *Concentrated radium salts.* Tables 4, 5 and 6 contain the necessary data for the estimation of salt-absorption corrections when the type and density of the salt and the internal diameter of the container are known. Consider, for example, a cylindrical tube of internal length 8 mm. and internal diameter 4 mm. containing 200 mg. Ra element in the form of radium sulphate which completely fills the tube. The weight of the salt is 285 mg., the density (ρ) is 2.84 g./c.c., the mass-absorption coefficient (μ/ρ) 0.055 and the linear absorption coefficient

μ is 0.156 cm.^{-1} . The value of μd ($d = 4 \text{ mm.}$) is thus 0.0624 and the salt-absorption correction interpolated from table 5 is 2.7% . When the corrections are of this order of magnitude, a 5% change in the value of μ changes the correction by 0.1 and the radium-content value by 1 part in 1000. Table 7 gives the corrections applicable to full tubes of radium sulphate for packing densities of $2, 2.5$ and 3 g./c.c. The corresponding corrections for tubes of radium bromide are a little less and those for radium chloride and radium carbonate a little greater than the corrections given in table 7.

Table 7. Percentage salt-absorption corrections for full tubes of radium sulphate. Lead filter 0.5 cm. thick.

Internal diameter of tube (mm.)	Percentage correction		
	$\rho = 2 \text{ g./c.c.}$	$\rho = 2.5 \text{ g./c.c.}$	$\rho = 3 \text{ g./c.c.}$
1.0	0.5	0.6	0.7
3.0	1.4	1.8	2.1
6.0	2.8	3.6	4.2
8.0	3.8	4.7	5.7

6.2. *Radioactive luminous compounds.* Radioactive luminous compound consists of a mixture of zinc sulphide with radium or with radium and mesothorium, the radioactive material being present in concentrations of the order of a hundred microgrammes of radium element or its equivalent per gramme of compound. Paterson, Walsh and Higgins (1917) determined the absorption in zinc sulphide from the results of gamma-ray measurements before and after mixing a known quantity of radium salt with zinc sulphide and also by surrounding a sealed tube of radium salt with a known thickness of zinc sulphide. By the former method the absorption coefficient was found to be 0.3 cm.^{-1} and by the latter 0.092_5 cm.^{-1} . It was later (1921) suggested by Owen and Fage that the higher value could have been due to the imperfect sealing of the tube containing the mixture of radium salt and zinc sulphide. These authors found the absorption coefficient to be 0.101 cm.^{-1} , the value being the same, within the limits of experimental error, for zinc sulphide mixed with radium as for zinc sulphide alone. The mass-absorption coefficient corresponding to the results of Owen and Fage is 0.050 , i.e. greater than the present author's value, 0.030 . It seems that different scattering conditions* may account at least in part for the divergent values. A contributory cause may be alterations in the materials and disposition of the measuring apparatus which have been introduced since the earlier measurements were made.

The corrections for full tubes of luminous compound 3 cm. or less in diameter,

* A value approaching 0.050 was obtained by the author when the cross-section of the absorbing specimen (zinc sulphide enclosed in a flat-walled vessel) was only just sufficient to screen the ionization chamber from the radium cell, the latter being in the "end-on" position with respect to the chamber. Correspondingly high values were also obtained in the case of other powdered materials. This arrangement of source and absorber decreases the amount of radiation scattered into the ionization chamber by the absorbing specimen, partly on account of the reduced scattering area and partly on account of the partial separation of the source and the specimen (Tarrant, 1931/32.)

based on the mass-absorption coefficient 0·03 for zinc sulphide, are given sufficiently accurately by $c_s = 1\cdot3\rho d$, where c_s is the percentage correction, ρ is the density of the compound in g./c.c. and d is the internal diameter of the tube in cm. The additional correction for the absorption in the walls of the glass tube in which such compound is usually enclosed for measurement purposes is 0·8% per mm. of wall thickness for thicknesses up to 2 mm. The same corrections apply when mesothorium is present in addition to radium, since the absorption of the gamma rays from mesothorium and its decay products is only slightly different from that of the gamma rays from radium.

6.3. Radium concentrates. "Radium concentrates" is the term generally applied to radium-bearing products of refining operations. Such products usually contain several milligrammes of radium element per kilogramme of material, the latter comprising a high proportion of barium and frequently some lead, the remaining constituents being elements of low atomic number. A convenient sample for radium-content tests is one hundred grammes accommodated in a sealed glass cylinder about 5 cm. in diameter and 10 cm. long. The mass-absorption coefficient of the material depends on its composition, and is derived by using the values given in table 3, or by using the empirical formula (2) for the various constituents of the material. A number of such samples sent recently to the Laboratory for radium-content tests contained 35% to 45% barium oxide (BaO) and 5% to 15% lead oxide (PbO), the remainder consisting of elements of low atomic number. The mass absorption coefficients of the samples derived by using (2) ranged from 0·034 to 0·038 and the salt-absorption corrections from 6% to 8%.

6.4. Radium-beryllium neutron sources. Radium-beryllium neutron sources consist of an intimate mixture of radium salt with beryllium powder in the proportion of about 100 mg. of radium element to several hundred mg. of beryllium. The mass-absorption coefficient of beryllium may be assumed to be the same as that for the elements of low atomic number in table 3, i.e. 0·032. Curtis (1939) has determined experimentally the total wall- and salt-absorption correction for a neutron source consisting of 1237 mg. of beryllium and 139·7 mg. of radium element (in the form of radium sulphate) enclosed in a brass cylinder of internal diameter 8 mm., internal length 24·5 mm. and wall thickness 1 mm. Assuming the brass to be of density 8·55, the wall-absorption correction, based on the results given in this paper, is 3·0%. The salt-absorption correction is 1·4%, the total correction being thus 4·4%. Curtis obtained the value 5·1% by radium-content measurements before and after mixing the radium salt and the beryllium. The difference between these two values is probably due in part to differences in the measuring equipment in the two cases.

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THEORETICAL SHAPE OF THE COMPTON PROFILE FOR ATOMS FROM H TO Ne

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ABSTRACT. Closed analytical expressions are obtained for the shapes of the modified Compton lines scattered from the elements H to Ne, in atomic form. The widths of the Compton lines are calculated for these atoms, and conditions of resolution from the unmodified lines are obtained. Certain errors in other work on this subject are noted and corrected. The width of the Compton line, as determined experimentally, for diatomic molecules is about 15 to 25 % greater than for isolated monatomic atoms.

§ 1. INTRODUCTION

IT is well known that a study of x-ray scattering enables us to determine the spatial distribution of electrons within an atom: in this way the wave-mechanical predictions have been fully confirmed. It is, however, also possible to determine the velocity distribution, and again this may be compared with the theoretical predictions. This is achieved by a study of the shape of the Compton modified line. For if a homogeneous beam of x rays falls on an atom in which all the electrons are at rest, the Compton line should have a single modified frequency. But if the electrons are moving there is a Doppler effect, related to the velocities of the electrons; this causes the modified line to spread out and become a band, whose profile determines the velocity distribution. This is the photon theory of Jauncey and DuMond (DuMond, 1933), which has been shown by Burkhardt (1936) and Schnaitd (1934) to give effectively the same results as the complete wave-mechanical theory due to Wentzel and Waller.

Recent improvements in x-ray technique (Kappeler, 1936) enable an accurate determination of the Compton profile to be made. We therefore present in this paper the theoretical profiles to be expected for the atoms H to Ne. The general appearance of these curves has, indeed, already been calculated by Kirkpatrick, Ross and Ritland (1936, referred to hereafter as K.R.R.). These calculations, however, are not satisfactory; there are three reasons for this. In the first place relatively inaccurate wave-functions were used, in which there was not sufficient flexibility; in the second place it was assumed that the individual atomic orbitals were mutually orthogonal, when in fact (see later) they are not; and finally there appear to be discrepancies in the actual calculated values, whose origin we have not been able to discover. Thus Hicks (1937) has calculated the Compton profile for He using various approximate wave-functions. We have performed some of his calculations independently, and agree with him; but we disagree with the values of K.R.R., which are quoted by Hughes and Mann (1938). An even more serious disagreement occurs for atomic H, where the values (quoted by Hughes and Starr, 1938, who were equally puzzled by the discrepancy) given by Hicks are reproduced in our own work; they differ from the K.R.R. values by as much as 25% in the important part of the curve. We find a similar disagreement with the carbon curves, though we are unable to explain why the K.R.R. values are incorrect. In view of these differences we have thought it worth while to recalculate the shape of the Compton profile for all the atoms H to Ne, taking advantage of the fact that more accurate wave-functions are now available (Duncanson and Coulson, 1944).

These calculations have another importance, for Hughes and Mann (1938) have shown that the distribution of inelastically scattered electrons has the same form as the function describing the Compton profile. Indeed, one reason for the present calculations is that accurate experiments of this kind have been made for H_2 and He, and their conclusions agree very precisely with those predicted theoretically.

§ 2. METHOD OF CALCULATION

Our method of calculation follows closely that which has been used in an earlier series of papers by the present authors (for a complete list of references see Duncanson, 1943). Thus let p be the momentum of an electron in the atom, and $I(p)$ the mean radial distribution function. This means that $I(p)dp$ is the probability that p has a magnitude between p and $p+dp$. Obviously

$$\int_0^\infty I(p)dp = 1. \quad \dots \dots (1)$$

$I(p)$ may be calculated at once if we know the momentum wave-function $\chi(p)$. Thus, if there is only one electron,

$$I(p) = \int \chi(p)\chi^*(p)p^2 d\omega, \quad \dots \dots (2)$$

where $d\omega$ is an element of solid angle for p . The extension required for more than one electron is obvious. Now the momentum wave-functions $\chi(p)$ are not known directly, but may be obtained from the space wave-functions $\psi(r)$

by the Dirac transformation theory. Thus, for one electron, using atomic units,

$$\chi(p) = (2\pi)^{-3/2} \int e^{-ip \cdot r} \psi(r) dr. \quad \dots \dots (3)$$

Again, as in (2), the extension to more electrons is straightforward.

The actual shape of the Compton profile depends on the incident wave-length λ_i and the angle of scattering θ . But all angles and wave-lengths are included in one single formula in the following way. Let λ_c be the peak of the modified line, so that the familiar relation holds:

$$\lambda_c = \lambda_i + 2\gamma \sin^2 \theta / 2, \quad \dots \dots (4)$$

where

$$\gamma = h/m_0 c = 0.0243 \text{ Å.}$$

Then choose a new wave-length λ^* defined by

$$2\lambda^* = \{\lambda_c^2 + \lambda_i^2 - 2\lambda_c \lambda_i \cos \theta\}^{1/2}. \quad \dots \dots (5)$$

In most cases effectively

$$\lambda^* = \lambda_i \sin \theta / 2. \quad \dots \dots (6)$$

Next let J be the intensity of the Compton band at a displacement l from λ_c , and let us introduce the variable

$$q = cl/2\lambda^*, \quad \dots \dots (7)$$

where c is the velocity of light (value 137 in atomic units). Then J is a function merely of q , with its peak at $q=0$, symmetrical about the peak, and defined by

$$J(q) = \frac{1}{2} \int_q^\infty \frac{I(p) dp}{p}. \quad \dots \dots (8)$$

Previous workers have always used an arbitrary constant k instead of $\frac{1}{2}$ in this formula, but we can show that $\frac{1}{2}$ is necessary if we want the total area below the $J(q)$ curve to be unity. In that case we can speak of a normalized profile. For using (8) the area under the $J(q)$ curve is

$$\begin{aligned} \int_{-\infty}^{+\infty} J(q) dq &= 2 \int_0^\infty J(q) dq = \int_0^\infty \int_q^\infty \frac{I(p) dp}{p} dq \\ &= \int_0^\infty \int_0^p \frac{I(p) dp}{p} dq dp \\ &= \int_0^\infty I(p) dp \\ &= 1, \text{ from (1).} \end{aligned}$$

Equation (8) enables us to calculate the Compton profile, since (2) and (3) have already provided us with a knowledge of $I(p)$.

§ 3. WAVE-FUNCTIONS USED

The best available wave-functions for the series of atoms concerned are those recently described by Duncanson and Coulson (1944). They are formed by suitable linear sums of determinants compounded of the separate orbitals:

$$\begin{aligned} \psi(1s) &= \sqrt{(\alpha^3/\pi)} e^{-\alpha r}, \\ \psi(2s) &= \sqrt{(\mu^5/3\pi N)} [re^{-\mu r} - (3A/\mu) e^{-\mu r}], \\ \psi(2p_0) &= \sqrt{(\gamma^5/\pi)} r \cos \theta e^{-\gamma r}, \\ \psi(2p_{\pm}) &= \sqrt{(\gamma^5/2\pi)} r \sin \theta e^{-\gamma r \pm i\phi}. \end{aligned} \quad \dots \dots (9)$$

Values of the parameters $\alpha (\equiv \mu a)$, $\beta (\equiv \mu b)$, $\gamma (\equiv \mu c)$, μ , A and N are given for each separate atom. The states of the atoms with which we are concerned are

H	$(1s)^2 S$,	He	$(1s)^2 1S$,	Li	$(1s)^2 (2s)^2 S$,
Be	$(1s)^2 (2s)^2 1S$,	B	$(1s)^2 (2s)^2 (2p)^2 P$,	C	$(1s)^2 (2s)^2 (2p)^2 3P$,
N	$(1s)^2 (2s)^2 (2p)^3 4S$,	O	$(1s)^2 (2s)^2 (2p)^4 3P$,	F	$(1s)^2 (2s)^2 (2p)^5 2P$,
Ne	$(1s)^2 (2s)^2 (2p)^6 1S$.				

Other states, and particularly solid or crystal states, would require different wave-functions, and the Compton profiles would not be given by our present calculations. But for atomic states involving the same numbers of s and p orbits, differently arranged, it appears that the profiles would be almost unaffected. Previous to the availability of (9) it had been common to use Slater wave-functions (1930), and we have therefore carried through some of our calculations for both types for comparison. Slater's wave-functions are particular cases of (9) with $A=b=0$, $\mu=\gamma$, $N=1$, and with different values of the exponents α and μ .

§ 4. FORMULAE

If all the $1s$, $2s$, $2p$ orbitals are mutually orthogonal, it is not hard to show (Duncanson and Coulson, 1941) that $I(p)$ is simply the sum of a suitable number of separate functions $I_{1s}(p)$, $I_{2s}(p)$, $I_{2p}(p)$, and consequently, from (8), that $J(q)$ is itself the sum of a corresponding number of functions $J_{1s}(q)$, $J_{2s}(q)$, $J_{2p}(q)$. This illustrates a contention of Hicks (1940) that the over-all line shape for the whole atom is the sum of the component line shapes of each type of electron.

We omit the details of the calculations of the integrals, but it follows from (2), (3), (8) and (9) that

$$\begin{aligned}
 I_{1s}(p) &= 32\alpha^5 p^2 / \pi(p^2 + \alpha^2)^4, \\
 I_{2s}(p) &= \frac{32\mu^5 p^2}{3N\pi} \left\{ \frac{3\mu^2 - p^2}{(p^2 + \mu^2)^3} - \frac{3A}{\mu} \frac{\beta}{(p^2 + \beta^2)^2} \right\}^2, \\
 I_{2p}(p) &= 512\gamma^7 p^4 / 3\pi(p^2 + \gamma^2)^6, \\
 J_{1s}(q) &= 8\alpha^5 / 3\pi(q^2 + \alpha^2)^3, \\
 J_{2s}(q) &= \frac{16\mu^5}{3N\pi} \left\{ \frac{5q^4 - 20q^2\mu^2 + 23\mu^4}{30(q^2 + \mu^2)^5} + \frac{3\beta^2 A^2}{2\mu^2(q^2 + \beta^2)^3} \right. \\
 &\quad \left. - \frac{3\beta A}{\mu(\mu^2 - \beta^2)^4} \left[2(5\mu^2 + \beta^2) \log \frac{q^2 + \beta^2}{q^2 + \mu^2} + \frac{2\mu^2(\mu^2 - \beta^2)^2}{(q^2 + \mu^2)^2} \right. \right. \\
 &\quad \left. \left. + (\mu^2 - \beta^2) \left(\frac{3\mu^2 + \beta^2}{q^2 + \beta^2} + \frac{7\mu^2 + \beta^2}{q^2 + \mu^2} \right) \right] \right\}, \\
 J_{2p}(q) &= \frac{32\gamma^7}{15\pi} \frac{5q^2 + \gamma^2}{(q^2 + \gamma^2)^5}. \quad \dots \dots \dots (10)
 \end{aligned}$$

In this way a closed analytical expression is obtained for the shape of the Compton line.

If the component orbitals are not orthogonal, as occurs with the Slater wave-functions, neither $I(p)$ nor $J(q)$ is of the simple form represented by sums of contributions from each electron, and new terms appear, which we do not need to describe here, due to the non-orthogonality of $\psi(1s)$ and $\psi(2s)$. In this case

the calculations may be much simplified by defining a new $2s$ orbital of the form $\psi(2s) + m\psi(1s)$, and choosing m so that this is orthogonal to $\psi(1s)$. We may describe this as orthogonalizing the Slater wave-functions (Slater, 1932; Wilson, 1933).

It may perhaps be mentioned here that the wave-functions used by K.R.R. were hydrogen-like. That is to say, the $2s$ and $2p$ orbitals, like the $1s$ orbital, were those to be expected for a single electron moving round an arbitrary central charge, whose value was found by using the rules (but not the wave functions) developed by Slater. These orbitals are only orthogonal if the same effective nuclear charge is used for all electrons, except that if their l and m quantum numbers differ, they are orthogonal by symmetry. With the values used by K.R.R. and, later, by Burkhardt (1936), a different effective charge is used for the K and L shell electrons. One possible, though, as we believe, small, source of error arises in this respect.

§ 5. RESULTS AND DISCUSSION

We show in figure 1 the normalized $J(q)$ curves for H, He, Li, C and Ne; and in figure 2 the curves for Li to Ne adjusted so that the peak value is unity in each case. This enables a better comparison to be made. Only half the profile is shown since, to our present approximation, the complete profile is symmetrical. The corrections to be made for relativity and binding are small, and Burkhardt

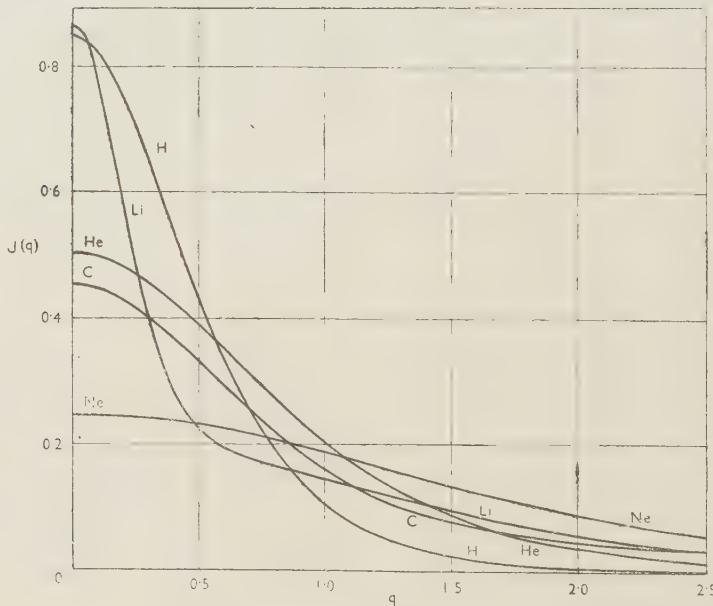


Figure 1.

(1936) has shown that they exert only a small effect upon the symmetry of the profile. The general features of these curves are similar to those described by K.R.R. : that is to say, s electrons give sharp profiles and p electrons wider ones, and as we proceed along a row of the periodic table, the profile becomes steadily broader, narrowing again for the alkali metal that starts the new sequence.

The shapes of the curves are conveniently summarized by the total width at half-maximum. The corresponding q -values, written Δq , are given in the first row of table 1. The width may be expressed on a wave-length scale by recalling (equations (6) and (7)) that $q = c\lambda_i / 2 \sin \theta/2$, and that the width at half-maximum is Δl , where $\Delta l = 2(\lambda_i/c) \sin \theta/2 \Delta q$. In the bottom row of the

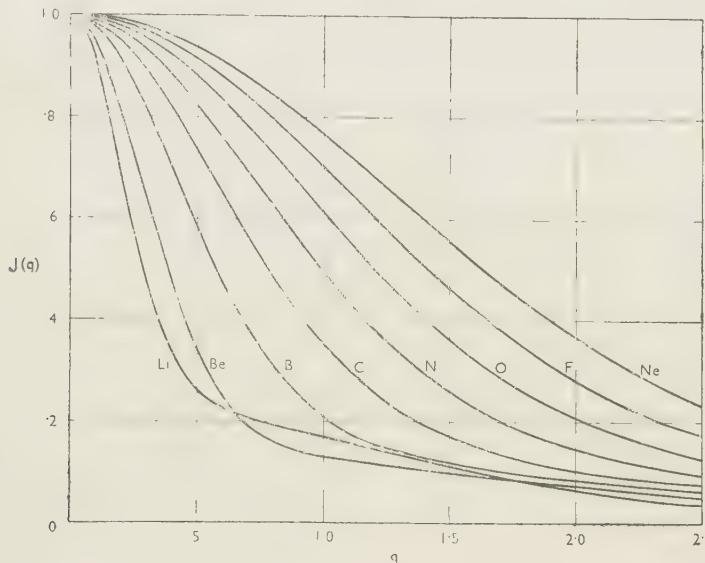


Figure 2.

table we give the corresponding values of Δl for $\theta = 180^\circ$ and $\lambda_i = 707.6$ x.u. (Mo $K\alpha$ radiation.) The gradual increase of Δl as we go along the periodic table from Li to Ne is clearly shown. Wollan's contention (1934) that all atoms from $Z=3$ to $Z=13$ should have $\Delta l = 22$ x.u. is evidently not correct, even though allowance be made for possible inadequacies in our theoretical wave-functions.

Table 1. Half-widths of Compton profiles

	H	He	Li	Be	B	C	N	O	F	Ne
Δq	1.02	1.74	0.57	0.77	1.15	1.57	1.98	2.40	2.84	3.27
Δl (x.u.) Mo $K\alpha$	11	18	5.9	8.0	12	16	20	25	29	34
$\theta = 180^\circ$										

Let us consider what experiments are available with which to check the Δl and Δq values of table 1. In the first place the calculated values are for monatomic systems; this limits a strict comparison to He and Ne. For neon (Burkhardt, 1936; Kappeler, 1936) the experimental value is $\Delta l = 32$ x.u., so that $\Delta q = 3.1$, in excellent agreement with theory. For He, DuMond and Kirkpatrick (1937) obtain an experimental value $\Delta l = 16$ x.u., giving $\Delta q = 1.5$. This, indeed, was the value deduced theoretically by Hicks (1937) using much more involved wave-functions. As there are only two electrons in He, it is possible to refine the wave-functions considerably by explicit inclusion of the distance between the electrons. Hicks shows that this reduces Δq from about 1.7 to 1.5. As the mutual

electron repulsion is relatively more important in He than in the other atoms concerned, we may reasonably expect a smaller correction term in the rest of the table. It may be mentioned here also that Hughes and Mann (1938), in electron-scattering experiments, obtain effectively the same Δq for He as DuMond and Kirkpatrick in their x-ray experiments.

It thus appears that our curves fit satisfactorily with experiment for He and Ne. There appear to be no other experiments directly suitable for comparison. The pioneer work of Woo (1926) does indeed give shapes for these atoms, and in general terms they agree with figure 2. But as K.R.R. say, Woo "sacrificed resolving power in favour of intensity", and as a result "all details of the shape were missed". There is a further difficulty in that Woo necessarily used solid scatterers, whereas our formulae relate to free atoms. In a solid, as the experiments of DuMond with graphite show quite clearly (DuMond, 1933, figure 33), the velocities of the electrons are greater than in the free atom, and the Compton profile is correspondingly broadened.

It is however possible to compare our table of Δq values with the results of experiments on diatomic molecules. The effect of molecular binding is to increase the mean momentum of the electrons, and hence to broaden the Compton profile. Thus Duncanson and Coulson (1941) and Coulson and Duncanson (1942) have shown that the CH_4 profile is about 5% wider than that corresponding to $\text{C} + 4\text{H}$; and Duncanson (1943) shows that much the same occurs for N_2 and Li_2 , the increase still being of this order. Experimentally, Kappeler (1936) gives $\Delta q = 2.7$ for O_2 and $\Delta q = 2.5$ for N_2 , where we should have expected 2.4 and 2.0 respectively for free atoms. The enhanced value of Δq is clearly shown, though its size is rather more than we should have anticipated. The increase is, however, actually as large as claimed, for Hughes and Starr (1939) get just the same value for N_2 with electron scattering. In the case of H_2 , Hicks (1937) computes $\Delta q = 1.17$, about 14% greater than the atomic value, and Hughes and Starr (1938) get an experimental value about 11% wider than this. It would be very valuable to have accurate x-ray values for H_2 . At present it appears that by forming a diatomic molecule, the width of the Compton profile is increased by about 15 to 25%.

The only other reasonably valid experimental result which we can utilize is Kappeler's value (1936) for acetylene carbon black. This gives $\Delta q = 2.0$, again about 25% greater than the atomic value. This type of carbon is probably more nearly molecular than crystalline, so that the value is about what might have been expected.

If we consider pure crystals, the width is much greater than for free atoms. Thus with graphite there is about 75% excess, and with Be 140% excess above the atomic values. It is evidently unreasonable to attempt any comparison; the profile needs to be calculated entirely differently, as was done for C and Be by Bloch (1934). The situation is even worse with metallic Li (Kappeler, 1936).

With longer incident waves the Compton profile broadens and finally merges into the unmodified line. The curves in figure 2 may be used to indicate the conditions under which the two lines may be resolved. It is well known (Wollan, 1933) that for light elements the modified line is stronger than the unmodified,

and that for heavy elements the unmodified line is the stronger. No completely rigorous discussion of resolving the two can be given without taking this variation into account, but a rough criterion can be made by supposing that if at the point midway between the maxima of the two bands the intensity of the Compton band is less than one-half of its maximum value, then resolution is possible. This convention, which is almost certainly too severe, probably by a factor of nearly two, will at least indicate the order of wave-length necessary for resolution, and show how it varies with the atom concerned.

Now the position of the unmodified line ($\lambda = \lambda_i$) is given on the q -scale by

$$q = \frac{c(\lambda_c - \lambda_i)}{2\lambda_i \sin \theta/2} = \frac{c\gamma \sin \theta/2}{\lambda_i} \text{ approx.} \quad \dots \dots (11)$$

So at the mid-point $q = \frac{c\gamma \sin \theta/2}{2\lambda_i}$, and our criterion requires that for this value of q , $J(q) < \frac{1}{2}J(0)$. This gives upper limits for $\frac{\lambda_i}{\sin \theta/2}$, which are shown (in Å.) in table 2. It appears that large angles of scattering are less favourable for this resolution, but the effect is not great unless θ is small, and then all the displacements are so small as to decrease the accuracy of measurement on account of scatter. This table also shows how the resolution decreases for heavier atoms along each row of the periodic table.

Table 2. Maximum values (in Å.) of $\frac{\lambda_i}{\sin \theta/2}$ for resolution of modified and unmodified lines

H	He	Li	Be	B	C	N	O	F	Ne
3.3	1.9	5.9	4.2	2.9	2.1	1.7	1.4	1.2	1.0

In conclusion, we may refer briefly to two other related matters. In the first place, as figures 1 and 2 show, the shape of the Compton profile varies from atom to atom. This variation is not only in width, but also particularly in the relative importance of the "leg" at the base. This means that the approximate shape $y = a/\left\{1 + \left(\frac{x}{b}\right)^2\right\}$ assumed by Hoyt (1932), and employed subsequently by other workers, is only a fair representation over the greater part of the band for atoms where the effect of the s electrons in sharpening the profile is counterbalanced by a larger number of p electrons broadening it. In the cases of Li and Be in particular, and presumably also for other elements in the same columns of the periodic table, the presence of the tail will complicate the separation of the contributions to the full profile that arise from satellite lines, as, e.g., $K\alpha_1$ and $K\alpha_2$ doublet, if Hoyt's formula is used. The method used by DuMond (1933, p. 31) appears more suitable.

Our final comment concerns the use of orthogonal orbitals, which we referred to at the end of § 4. Since the $2p$ orbital is by symmetry orthogonal to the $1s$ and $2s$ orbitals, we are here only concerned with the lack of orthogonality between the $1s$ and $2s$ wave-functions. We have made detailed calculations of this effect for one or two atoms. For convenience we used the somewhat simpler wave-functions of Slater rather than the more elaborate ones used in the earlier

part of this work. This should not, however, greatly affect the error due to neglect of non-orthogonality. It appears from our work that an alteration not exceeding 5% is made in any one value of Δ ; the result of neglecting non-orthogonality is to widen the theoretical profile very slightly. Table 3 shows for the atoms Li and C the widths Δq at half-maximum value when (a) the non-orthogonality is neglected and (b) when the 2s orbital is suitably orthogonalized. The effect on the width is surprisingly small, and suggests that it should be possible to calculate sufficiently accurate profiles for other elements in the same simple way, without recourse to the labour of orthogonalization.

Table 3. Effect of non-orthogonality

Atom	Δq , neglecting non-orthogonality	Δq , allowing for non-orthogonality
Li	0.571	0.567
C	1.574	1.562

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ACHROMATIZED PLATE-MIRROR SYSTEMS

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ABSTRACT. A variant of the Schmidt-Cassegrain optical system is described in which the single aspheric plate is replaced by two plates, of different glasses and opposite asphericities, whose colour-errors compensate each other. The use of two plates makes it possible to obtain not only apochromatism but also flat-fielded anastigmatism with both mirrors spherical. Design data are given for such two-sphere two-plate anastigmats and their distortion is shown to be small. Next, the effect of relaxing the strict anastigmatism condition is considered and it is shown that the admission of a small amount of Seidel astigmatism leads to a large extension of the range of available systems. Finally two aplanat types are selected which seem well suited to astronomical application.

§ 1. INTRODUCTION

THE colour-error in a Schmidt-Cassegrain camera, chiefly chromatic variation of spherical aberration, is small enough to be tolerated in systems of moderate size. For example, in an F/2 system of focal length 13 inches, constructed with a borosilicate crown plate, the diameters of the red and blue confusion circles on axis are each about 0·0015 inch when the plate is figured in green mercury light, while in an F 2·5 system of the same focal length their size is only half this amount.

In larger systems, the question of colour correction becomes important at apertures above F/3. Evidently two plates, of different glasses, are needed to achieve it; these plates must be of opposite asphericities and (if they are both to lie in the parallel incoming beams) of strengths inversely proportional to their dispersions. J. G. Baker (1940), in his paper "A family of flat-fielded cameras equivalent in performance to the Schmidt camera", proposed to use two such plates in contact, and A. Warmisham (1941, 1943) has described systems in which each of two spherical mirrors is corrected by a plate placed at its (actual or imaged) centre of curvature.* From the point of view of the general theory of plate-mirror systems, the condition that the plates should be in contact, or that they should each anastigmatize one spherical mirror, appears a somewhat arbitrary limitation, and it is natural to ask whether improved types of two-plate Schmidt-Cassegrain systems may not become available when it is removed. The main object of the present paper is the discussion of this question.

In § 2 we show how, by the use of two spherical mirrors and two aspherical plates, a two-parameter family of flat-fielded anastigmats can be constructed, apochromatic and satisfying the exact sine condition. These systems seem to offer some advantages in ease of construction over the achromatized Baker cameras; they involve only two aspherical surfaces, as compared with three in

* Warmisham does not mention colour correction in the first of these patents, but his examples allow it by a suitable choice of glasses.

the Baker systems (or four in Baker's type D). Further, the aspherized surfaces are both pseudo-flats, which are easier to figure than more sharply curved surfaces.

In § 3 we consider the effect of allowing small departures from strict Seidel anastigmatism, such as are required to balance the higher errors over a finite field, and show that the range of practical anastigmats is considerably wider than is suggested by the Seidel theory alone.

§ 2. ANASTIGMATS

The system to be discussed consists of two aspheric, nearly plane-parallel plates, in general of different glasses, and two spherical or figured mirrors, namely a large concave primary and a small convex secondary. The arrangement is shown in figure 1. The light from the object-surface, supposed infinitely distant, passes through the two plates P , P' , and is reflected from the surface of the concave primary M_1 on to the convex secondary M_2 . There it is again

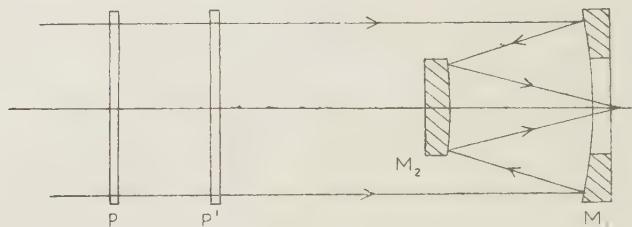


Figure 1.

reflected and comes to a focus near or just behind the primary, which is pierced with a central hole in the latter case to allow the rays to pass. In short, the system is an extension of the Schmidt-Cassegrain type* in which the single aspheric plate of the ordinary Schmidt-Cassegrain is replaced by two plates, at different distances in front of the primary. We shall refer to it as a two-plate Schmidt-Cassegrain system.

The Seidel errors of such a system can be most conveniently investigated by the method of plate-diagram analysis. Let

A, B, Γ, Γ' be the figuring depths on M_1, M_2, P, P' respectively, expressed in terms of parabolic correction of M_1 as unit;

σ, σ' the distances of P, P' in front of M_1 , expressed in terms of the paraxial focal length f_1 of M_1 as unit;

ξ the ratio f_2/f_1 of the paraxial focal length (taken positively) of M_2 to that of M_1 ;

$\delta = d/f_1$ the separation between the mirrors, expressed in terms of f_1 as unit; $q = 1 - \delta$ the "minimum obstruction ratio" for the on-axis pencil.

Then, assuming for the present that the aperture-stop is on the primary, the system possesses the plate-diagram shown in figure 2. From this the aplanatism conditions can be read off in the form

* See *Mon. Not. R. Astr. Soc.* **104**, 48–64 (1944). A knowledge of the contents of this paper is assumed in what follows.

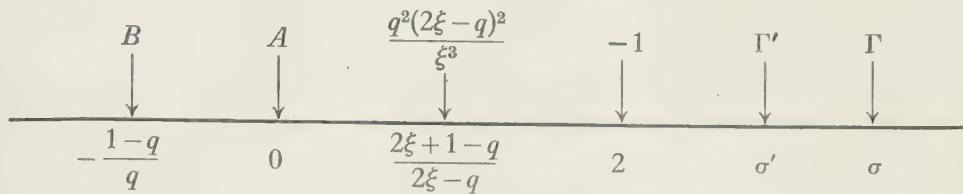


Figure 2.

$$(Spherical aberration) \quad A + B + \Gamma + \Gamma' + \frac{q^2(2\xi-q)^2}{\xi^3} - 1 = 0. \quad \dots \dots (1)$$

$$(Coma) \quad -\frac{1-q}{q}B + \sigma\Gamma + \sigma'\Gamma' + \frac{q^2(2\xi-q)(2\xi+1-q)}{\xi^3} - 2 = 0, \quad \dots \dots (2)$$

and the astigmatism of the system is measured by the quantity *

$$\chi = \frac{\text{Astigmatism}}{\text{thin lens value}} = \frac{-\xi}{4(\xi-q)} \left[\left(\frac{1-q}{q} \right)^2 B + \sigma^2 \Gamma + \sigma'^2 \Gamma' + \frac{(2\xi+1-q)^2 q^2}{\xi^3} - 4 \right]. \quad \dots \dots (3)$$

In these systems, the image is formed at a distance

$$\left(\frac{2\xi-q}{\xi-q} q - 1 \right) f_1 \quad \dots \dots (4)$$

behind the pole of the primary, and the focal length

$$f = \frac{\xi}{\xi-q} f_1. \quad \dots \dots (5)$$

The Petzval curvature of the system

$$\frac{1}{\rho_P} = 2(D-C) = -\frac{1}{f_1} + \frac{1}{f_2} = \frac{1}{f_1} \cdot \frac{1-\xi}{\xi}, \quad \dots \dots (6)$$

and its distortion coefficient Δ is given by the equation †

$$-8\Delta = \sigma^3 \Gamma + \sigma'^3 \Gamma' - \left(\frac{1-q}{q} \right)^3 B + \frac{2\xi+1-q}{2\xi-q} \frac{(2\xi+1-q)^2 q^2 - 4\xi^2}{\xi^3}; \quad \dots \dots (7)$$

when the astigmatism is zero, the value of Δ is not changed by moving the aperture stop.

Two-sphere two-plate systems

Of special practical importance are the systems in which both mirrors are spherical and the colour-error is reduced to a negligible amount. We shall refer to these as the two-sphere two-plate systems. To obtain the aplanatism conditions for such a system, we set $A=B=0$ in equations (1), (2). We agree to choose the notation so that P denotes the stronger plate and P' the weaker, and we define

$$k = -\Gamma'/\Gamma;$$

* The physical meaning of χ is as follows : at an angle θ off axis in a system of focal length f the astigmatic difference is $\chi\theta^2 f$.

† Mon. Not. R. Astr. Soc. 104, 54 (1944), equation (13).

thus $0 < k \leq 1$ and k measures the ratios of the dispersions of the glasses required to give apochromatism. (1), (2), (3) then take the form

$$(1-k)\Gamma = P, \quad \dots \dots \dots (8)$$

$$(\sigma - k\sigma')\Gamma = Q, \quad \dots \dots \dots (9)$$

$$\chi = \frac{\text{Astigmatism}}{\text{thin lens value}} = \frac{-\xi}{4(\xi - q)} [(\sigma^2 - k\sigma'^2)\Gamma - R], \quad \dots \dots \dots (10)$$

where *

$$\left. \begin{aligned} P &= 1 - \frac{q^2(2\xi - q)^2}{\xi^3}, \\ Q &= 2 - \frac{q^2(2\xi - q)(2\xi + 1 - q)}{\xi^3}, \\ R &= 4 - \frac{q^2(2\xi + 1 - q)^2}{\xi^3}. \end{aligned} \right| \quad \dots \dots \dots (11)$$

The aplanatism conditions (8), (9) are together equivalent to the equations

$$\Gamma = \frac{P}{1-k}, \quad \sigma' = \frac{1}{k} \left[\sigma - \frac{(1-k)Q}{P} \right], \quad \dots \dots \dots (12)$$

and on substituting from (12) we obtain (10) in the form

$$\begin{aligned} \chi &= \frac{-\xi}{4(\xi - q)} \left[\frac{\sigma^2 - k\sigma'^2}{1-k} P - R \right] \\ &= \frac{-\xi}{4(\xi - q)P} \left[(Q^2 - PR) - \frac{1}{k}(P\sigma - Q)^2 \right] \\ &= \frac{-\xi}{4(\xi - q)P} \left[\frac{q^2}{\xi^3} (2\xi - 1 - q)^2 - \frac{1}{k}(P\sigma - Q)^2 \right]. \quad \dots \dots \dots (13) \end{aligned}$$

Since this can only vanish if $k > 0$, it follows that the plate-strengths must be of opposite sign in an anastigmat (or near-anastigmat). Equating the astigmatism to zero gives

$$\sigma = \frac{Q}{P} \pm \frac{1}{P} \sqrt{\frac{k}{\xi^3}} q(2\xi - 1 - q). \quad \dots \dots \dots (14)$$

It follows that all the two-sphere two-plate aplanats are given by (12) and all the two-sphere two-plate anastigmats by (12) together with (14). From (12) we have

$$\sigma' - \sigma = \left(\frac{1}{k} - 1 \right) \left(\sigma - \frac{Q}{P} \right) = \pm \left(\frac{1}{\sqrt{k}} - \sqrt{k} \right) \frac{q(2\xi - 1 - q)}{P\xi^{3/2}}. \quad \dots \dots \dots (15)$$

Thus to each choice of the three parameters q, k, ξ , subject to the inequalities

$$0 < q < 1, \quad 0 < k \leq 1, \quad 2\xi - 1 - q > 0, \quad \dots \dots \dots (16)$$

* P, Q and R are seen to be the sign-reversed contributions from the two power-surfaces (excluding figurings) to the spherical aberration $\sum_i A_i$, the coma $\sum_i A_i \sigma_i$ and the astigmatism $\sum_i A_i \sigma_i^2$ of the system.

correspond just two anastigmatic systems, namely, those given by

$$\left. \begin{aligned} \sigma &= \frac{Q \pm k^{1/2} q (2\xi - 1 - q) / \xi^{3/2}}{P}, & \Gamma &= \frac{P}{1-k}, \\ \sigma' &= \frac{Q' \pm k^{-1/2} q (2\xi - 1 - q) / \xi^{3/2}}{P}, & \Gamma' &= \frac{P}{1-1/k}, \end{aligned} \right\} \quad \dots\dots(17)$$

where both the upper signs or both the lower signs are to be taken.*

The two anastigmats (17) have the same plate strengths and the same plate separation, but the order of the plates is reversed on passing from one to the other. The overall length is less when the lower signs are taken; as starting point for an astrographic camera design, therefore, this second system is to be preferred.

Flat-fielded anastigmats

The necessary and sufficient condition that an anastigmat should be flat-fielded in Seidel approximation is that its Petzval curvature should be zero. Thus the flat-fielded anastigmats are the solutions of (12), (14), with $\xi = 1$. In this case the inequalities (16) reduce to

$$0 < q < 1, \quad 0 < k \leq 1,$$

and the second solution (17) to

$$\left. \begin{aligned} \sigma &= \frac{Q - k^{1/2} q (1 - q)}{P}, & \Gamma &= \frac{P}{1-k}, \\ \sigma' &= \frac{Q - k^{-1/2} q (1 - q)}{P}, & \Gamma' &= \frac{P}{1-1/k}, \end{aligned} \right\} \quad \dots\dots(18)$$

where now

$$P = 1 - q^2(2 - q)^2, \quad Q = 2 - q^2(2 - q)(3 - q). \quad \dots\dots(19)$$

Thus we have obtained a two-parameter family of flat-fielded anastigmats, apochromatic and with both mirrors spherical, which can in addition be made to satisfy the exact sine condition.†

Distortion in the flat-fielded anastigmats

Setting $B = 0$, $\xi = 1$ in (7), we obtain for the distortion coefficient Δ in the systems (18) the equation

$$-8\Delta = \sigma^3 \Gamma + \sigma'^3 \Gamma' - \frac{3-q}{2-q} R,$$

where R stands for the quantity $4 - q^2(3 - q)^2$,

$$\begin{aligned} &= \frac{[Q - (\sqrt{k})q(1 - q)]^3}{P^2(1 - k)} + \frac{[Q - (1/\sqrt{k})q(1 - q)]^3}{P^2(1 - 1/k)} - \frac{3-q}{2-q} R \\ &= \frac{1}{P^2} [Q^3 - 3Qq^2(1 - q)^2 + (\sqrt{k} + 1/\sqrt{k})q^3(1 - q)^3] - \frac{3-q}{2-q} R; \end{aligned}$$

i.e.
$$\Delta = -\frac{q^3(1 - q)^3}{8P^2} (\sqrt{k} + 1/\sqrt{k} - H), \quad \dots\dots(20)$$

* If $2\xi - 1 - q = 0$, i.e. if the mirrors are concentric, the two solutions run together into the single solution

$$\sigma = \sigma' = Q/P, \quad \Gamma = -\Gamma'/k = P/(1 - k),$$

a monocentric Schmidt-Cassegrain with achromatized plate.

† By essentially the same procedure as that outlined (for the case of a Baker B system) in *Proc. Phys. Soc. 55*, 494 (1943).

where

$$\begin{aligned} H &= \frac{1}{q^3(1-q)^3} \left\{ 3Qq^2(1-q)^2 - Q^3 + \frac{3-q}{2-q} P^2 R \right\} \\ &= 3 \frac{Q}{q(1-q)} - \left(\frac{Q}{q(1-q)} \right)^3 + \frac{3-q}{2-q} \left[\left(\frac{Q}{q(1-q)} \right)^2 - 1 \right]. \quad \dots \dots (21) \end{aligned}$$

Equation (20) has been derived on the assumption that the aperture-stop of the system is on the surface of the primary mirror M_1 . Since Δ is invariant under stop-shifting in a flat-fielded anastigmat, (20) remains valid when this restriction is removed.

Calculation shows that H is negative for $0.3 \geq q \geq 0.7$. Thus all the anastigmats in this q -range suffer from barrel distortion. Its amount decreases with increasing k ; table 1 shows, for selected values of q , the values Δ_1 , Δ_2 of Δ in the two cases $k = \frac{1}{2}$, $k = 1$; the corresponding values Δ_B in a Baker B system are included for comparison.

Table 1

q	H	Δ_1	Δ_2	Δ_B
0.4	-35.62	-0.187	-0.186	-0.205
0.45	-22.55	-0.177	-0.176	-0.198
0.5	-14.25	-0.167	-0.166	-0.191
0.6	-5.13	-0.145	-0.142	-0.174
0.7	-0.94	-0.120	-0.115	-0.152

We conclude that, in the region $0.4 \leq q \leq 0.7$, $\frac{1}{2} \leq k \leq 1$, the distortion is nearly independent of k , is slightly less than that of a Baker B system, and is given to within 10% accuracy by the approximate formula

$$\Delta \approx -0.08q.$$

At 3° off axis this corresponds in the case $q = 0.4$ to a fractional distortion of less than 0.05%.

The Warmisham systems

As a special case we may suppose that $k = q^2(2-q)^2$. Then (18) simplifies to

$$\sigma = 2, \quad \Gamma = 1; \quad \sigma' = \frac{3-q}{2-q}, \quad \Gamma' = -q^2(2-q)^2, \quad \dots \dots (22)$$

and we obtain a one-parameter family of flat-fielded anastigmats in which the outer plate is simply the Schmidt plate of M_1 in its normal position, and the inner is the image in M_1 of the Schmidt plate of M_2 .* Each plate thus anastigmatizes one mirror. The restriction $k = q^2(2-q)^2$, while unnecessary from our present point of view, is not a very serious limitation in practice. For example, to obtain $k = \frac{1}{2}$ and so allow on-axis colour correction with glasses chosen from an ordinary crown-flint pair, we need to choose $q = 1 - \sqrt{1 - \sqrt{k}} = 0.45$. This brings the image to a very convenient position $0.31f_1$ behind the front

* The Gauss image in M_1 of the centre of curvature of M_2 is at a distance

$$\frac{f_1(2f_2+d)}{2f_2+d-f_1} = \frac{2\xi+1-q}{2\xi-q} f_1 = \frac{3-q}{2-q} f_1$$

in front of M_1 .

surface of the primary. The focal length f is then $1.85f_1$ and the plate separation $\sigma - \sigma'$ is $0.35f_1 = \frac{1}{5}f$.*

When the chosen value of q is not close to 0.46, the general two-sphere anastigmats provide alternatives which offer some advantages over the corresponding Warmisham systems. When q is larger than 0.46 they offer the possibility of reducing the plate-strengths by giving to k a smaller value than $k_w(q) = q^2(2-q)^2$, while preserving full achromatism on axis. This reduction in plate-strength is obtained at the cost of a small increase in the overall length of the system. When q is smaller than 0.4, on the other hand, they allow on-axis achromatism to be maintained with conveniently available glass-types by giving to k a value greater than $k_w(q)$. This involves an increase in the plate strengths. A survey of the situation is provided by table 2, in which the constants σ , σ' , Γ , Γ' of anastigmats with $k = \frac{1}{2}$ are compared, for selected values of q , with those σ_w , σ'_w , Γ_w , Γ'_w of the corresponding Warmisham systems.

Table 2

q	σ	σ'	Γ	Γ'	σ_w	σ'_w	Γ	Γ'_w	$k_w(q)$	$f/f_1 = 1/(1-q)$
0.3	1.944	1.743	1.480	-0.740	2	1.588	1	-0.260	.2601	1.4286
0.4	1.973	1.685	1.181	-0.590	2	1.625	1	-0.410	.4096	1.6667
0.5	2.025	1.620	0.875	-0.438	2	1.667	1	-0.563	.5625	2.0000
0.6	2.108	1.532	0.589	-0.294	2	1.714	1	-0.706	.7056	2.5000
0.7	2.248	1.384	0.344	-0.172	2	1.769	1	-0.828	.8281	3.3333

§ 3. THE TWO-SPHERE TWO-PLATE APLANATS

The conditions (1) spherical aberration = 0, (2) coma = 0, (3) astigmatism = 0, (4) Petzval curvature = 0 of the Seidel approximation are to be replaced in practice by the conditions that these quantities should be small. This relaxation has only a small effect on the range of available systems so far as conditions (1), (2) and (4) are concerned, and we can therefore obtain a satisfactory survey of the useful systems by keeping the spherical aberration, coma and Petzval curvature strictly zero. With condition (3) the case is different; the admission of a small amount of astigmatism widens the range of possible systems considerably. It follows that, in making a survey of the useful two-sphere two-plate systems, it is necessary to consider not merely the Seidel anastigmats but the larger class of Seidel aplanats with zero Petzval curvature.† When this is done, an interesting result appears. Fixing q and k , let us consider the changes in the system as σ varies. To each value of σ corresponds a unique aplanat; for two values of σ the astigmatism vanishes and we recover the two anastigmats of § 2. In between these two values of σ the astigmatism is negative and small. Thus we obtain not two, but a whole range of useful systems. At the σ -point where the negative astigmatism reaches its worst value, the plates cross over, and when σ is greater than this value the weaker σ' -plate is the farther from the primary. At the cross-over value of σ , the system is equivalent to a two-sphere one-plate aplanat with achromatized plate.

* Of course it would be simpler, if our object were merely to derive the Warmisham systems to begin by combining a positive and a negative Schmidt system of equal mirror-curvatures. On imaging the plate of the negative system through into object-space we at once obtain (22).

† Not with flat "best field" in the Seidel sense, for reasons similar to those obtaining in the case of a two-sphere one-plate aplanat (*Mon. Not. R. Astr. Soc.* **104**, 61–62 (1944)).

To prove these statements, we set $\xi = 1$ in (12) and obtain the equations of the systems to be discussed in the form

$$\Gamma = \frac{P}{1-k}, \quad \dots\dots(23)$$

$$\sigma' = \frac{1}{k} \left[\sigma - \frac{(1-k)Q}{P} \right], \quad \dots\dots(24)$$

where P, Q are given by (19). Equation (13) now becomes

$$\chi = -\frac{1}{4(1-q)P} \left[q^2(1-q)^2 - \frac{1}{k}(P\sigma - Q)^2 \right]. \quad \dots\dots(25)$$

From (24) we have, as before,

$$\sigma' - \sigma = \left(\frac{1}{k} - 1 \right) \left(\sigma - \frac{Q}{P} \right). \quad \dots\dots(26)$$

For given q, k the values of Γ and $\Gamma' = -k\Gamma$ are fixed by (23), while σ' is given in terms of q, k and σ by (24). Thus the system is completely determined by choice of the parameter σ , which measures the distance of the stronger plate from the primary. Variation of σ is an operation which is very easily carried out experimentally; it consists merely in moving the plates P and P' along the axis of the system, the new position of P' being determined by (24). In this way the Seidel astigmatism of the system can be varied more or less at will. Of course the higher aberrations are also disturbed to some extent.

If, starting from the anastigmat (18), we increase σ by moving the plate away from the primary, it follows that from (26) the plate P' moves out also and decreases its distance from P , overtaking and passing it when $\sigma = Q/P$. From (25) we see that the ratio $\chi = \text{astigmatism (thin lens value)}$, which is negative when σ lies between the two anastigmat values $[Q \pm \sqrt{(k)q(1-q)}]/P$, attains its greatest negative value $-q^2(1-q)/4P$ when $\sigma = Q/P$, that is, when the plates are in the act of crossing over. Now for this value of σ the system is simply a two-sphere one-plate aplanat with achromatized plate. The astigmatism of such a system is so small when $q \leq 0.5$ that it is for all practical purposes anastigmatic, as will be seen from table 3.

Table 3

q	$\chi = -q^2(1-q)/4P$
0.3	-0.0213
0.35	-0.0299
0.4	-0.0407
0.45	-0.0542
0.5	-0.0714

It follows that throughout the σ -range between the two anastigmat values of σ , and for a short distance outside this range at either end, the two-sphere two-plate aplanats possess less astigmatism than a Schmidt-Cassegrain aplanat with the same value of q , and hence are for all practical purposes anastigmatic. We have supposed $q \leq 0.5$; this covers the astrographically valuable types.

Distortion

The value of the distortion coefficient now depends on the position of the aperture-stop. Let Δ_ζ denote its value when the stop is at a distance ζf_1 in front of the primary. When $\zeta = 0$, Δ_ζ reduces to the coefficient Δ of equation (7). In the general case we have *

$$\begin{aligned}\Delta_\zeta &= \Delta + \zeta f_1 \left(\frac{3}{8} \sum_P \alpha x^2 - \frac{1}{2} \sum_A \kappa \right) \\ &= \Delta + \zeta \left(\frac{3}{8} \sum_P A \sigma^2 - \frac{1}{2} f_1 \sum_A \kappa \right).\end{aligned}\quad \dots\dots(27)$$

Here $\sum_A \kappa = 0$, since the Petzval curvature is zero, while

$$\sum_P A \sigma^2 = -4\chi f_1/f,$$

by (3) and (5). Thus

$$\Delta_\zeta = \Delta - \frac{3}{2} \chi \zeta.\quad \dots\dots(28)$$

In practice, the value of ζ will usually be near to 1. For, assuming the system to be intended for ordinary astrographic use, it is very desirable to obtain as even an illumination of the field as possible, with the least possible sacrifice



Figure 3.

of aperture. This can be done by constructing the two plates and the large mirror all of the same diameter and inserting an aperture-stop, of slightly smaller diameter, half-way between the outer plate and the primary.† The diameter of this stop is chosen so that, at the edge of the designed field of 6° or 8° diameter, the outer edge of the effective aperture is not affected by vignetting.‡

In systems intended for astronomical search-photography, for example the detection of novae, it is better not to sacrifice light-gathering power by introducing an aperture-stop, but to allow the outer plate and the primary mirror to vignette

* Mon. Not. R. Astr. Soc. 104, 62 (1944), equation (28).

† It is tempting to pick out a class of "distortion-free" systems by the criterion that $\Delta_\zeta = 0$ when $\zeta = \frac{1}{2}\sigma$. But such a classification would have little practical value, because the empirical changes in the Petzval sum which are needed, at aperture near $F/2$, to flatten the field to the best advantage cause changes in Δ_ζ too great to be corrected by a small shift of the aperture-stop.

‡ Since $\cos^2 3^\circ = 1 - 1/400$ nearly, the illumination over a 6° diameter field will then fall by $\frac{1}{400}$ % from the centre to the edge of the field.

against each other. This applies with the greater force because the parts of the aperture which have to be sacrificed when uniform lighting is insisted upon are valuable regions of small "error slope", which contribute towards the central nucleus of the images near the edge of the field. These regions are shaded in figure 3, which shows the general appearance of the effective aperture.*

Two main types of system can now be selected as especially promising for astronomical application:

Type A. Systems in which σ is a little below the cross-over value Q/P . In these systems, the plates are near together but not in contact. Their separation makes it possible to satisfy the exact sine condition, and so eliminate the most important error (higher coma) of a two-sphere one-plate aplanat with achromatized plate, at a negligible cost in off-axis colour due to the shearing of the plates. Table 4 gives the Seidel data of six examples of this type; the fourth and fifth are illustrated in figure 4.

Table 4

q	k	σ	σ'	Γ	Γ'	χ	Δ	f/f_1
0.3	0.5	1.9	1.6553	1.4798	-0.7399	+0.0104	+0.1331	1.4286
0.35	0.5	2.0	1.8029	1.3330	-0.6665	-0.0100	-0.0046	1.5385
0.4	0.5	2.0	1.7398	1.1808	-0.5904	-0.0074	-0.0922	1.6667
0.4	0.6	2.1	1.9932	1.4760	-0.8856	-0.0301	+0.0430	1.6667
0.45	0.5	2.0	1.6638	1.0270	-0.5135	-0.0015	-0.1647	1.8182
0.45	0.6	2.1	1.9425	1.2837	-0.7702	-0.0325	-0.0720	1.8182

Type B. Systems of short overall length. To obtain these we have to choose σ as small as possible. The practical lower limit to σ is determined by

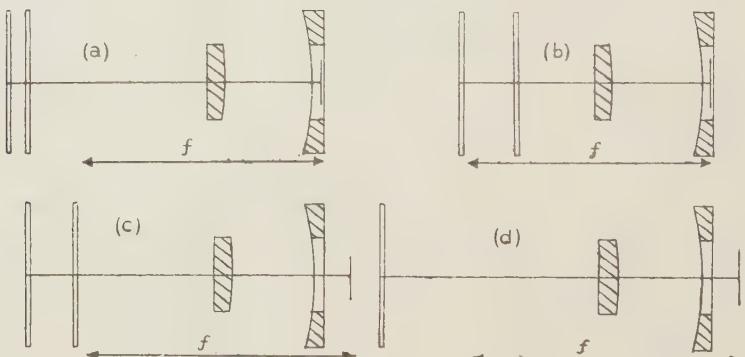


Figure 4.

- (a) Type A, $q=0.4$, $k=0.6$, $\sigma=2.1$.
- (b) Type B, $q=0.4$, $k=0.6$, $\sigma=1.67$.
- (c) Type A, $q=0.45$, $k=0.5$, $\sigma=2.0$.

(d) Baker B system, $q=0.45$, for comparison ; in this system the primary mirror is aspherical.

the astigmatism, which increases fairly rapidly when σ is decreased below its smaller anastigmat value. For a thin lens of twelve inches aperture the diameter

* The case actually illustrated is that of a system, of nominal aperture-ratio $f/2.5$, in which $\sigma=2$, $q=0.4$ and the diameter of the secondary mirror is half that of the primary, at 3° off axis. The effective aperture-ratio is $f/3$.

of the astigmatic confusion-circle 3° off axis is 0.015 inch at best focus. If we adopt one tenth of this value as the upper limit to the admissible Seidel astigmatism, we are led to impose the condition

$$|\chi| \leq 0.1,$$

which then determines the least permissible value of σ . Table 5 gives the Seidel data of five examples of type B systems; the third example is illustrated in figure 4.

Table 5

q	k	σ	σ'	Γ	Γ'	χ	Δ	f/f_1
0.3	0.5	1.6657	1.1866	1.4798	-0.7399	0.1000	0.2821	1.4286
0.4	0.5	1.7255	1.1908	1.1808	-0.5904	0.1000	0.0663	1.6667
0.4	0.6	1.6745	1.2840	1.4760	-0.8856	0.1000	0.2431	1.6667
0.45	0.5	1.7614	1.1866	1.0270	-0.5135	0.1000	-0.0276	1.8182
0.45	0.6	1.7065	1.2868	1.2837	-0.7702	0.1000	0.1160	1.8182

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ON GRÜNEISEN'S EQUATION FOR THERMAL EXPANSION

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ABSTRACT. The practical use of Grüneisen's relations as a means of calculating changes in volume from changes in thermal energy is discussed. The relation is often misquoted in an inaccurate and approximate form, and the correct form is described. The methods used for deducing the constants involved are discussed critically, and a simple and accurate method is described. For the cubic metals silver, copper and aluminium there is a very good agreement between the observed and calculated changes in volume between the absolute zero and a temperature of the order 2/3 of the melting point on the absolute scale, whilst for iron there is good agreement up to the temperature at which the magnetic transformation begins. For the hexagonal metals magnesium and zinc, the equation fails at very low temperatures if the substance has a negative coefficient of expansion in one direction (e.g. zinc), but is otherwise fairly satisfactory for the calculation of changes in volume up to a temperature of the order 2/3 of the absolute melting point.

1. INTRODUCTORY

In some recent work by the author, it was necessary to calculate the lattice spacings of metals in ranges of temperature for which the coefficient of expansion was unknown. This led naturally to the use of Grüneisen's equation connecting changes in volume with changes in thermal energy. Examination showed that confusion existed both as to the exact nature of

Grüneisen's relation and as to the accuracy which might be expected from its use. In this paper we examine these two points, and we present calculations for some metals for which both the coefficients of expansion and the specific heats are known accurately. We are concerned throughout with the practical use of Grüneisen's relation as a means for calculating changes in volume, and we do not attempt to discuss the theoretical implications.

§ 2. GRÜNEISEN'S RELATION

Grüneisen's relation is commonly described by saying that when the temperature of a body is altered, the change in volume is proportional to the change in thermal energy, provided that the substance is one for which the specific heat can be expressed in terms of a single Debye characteristic temperature, Θ . This definition lacks precision, and has been responsible for much confusion. It has, for example, led some authors to conclude that Grüneisen's relation implies a constant value for the ratio C_p/α , where α is the coefficient of expansion and C_p is the atomic heat at constant pressure; as we show later, this is a quite unjustifiable approximation of what Grüneisen's work really involves. Of the more precise definitions of Grüneisen's relation, we shall adopt the modification used by Simon and Vohsen. This may be expressed in the form

$$\frac{V_T - V_0}{V_0} = \frac{E_T}{Q_0 - kE_T}, \quad \dots \dots (1)$$

where V_0 and V_T are the volumes at the absolute zero and at T° K. respectively, and $E_T = \int_0^T C_v dT$. Q_0 is a constant whose derivation is discussed below, and k is a constant which is equal to $(\gamma + 2/3)$, where

$$\gamma = -V \frac{\partial V}{\partial T} / C_v \frac{\partial V}{\partial p}.$$

An alternative form of the equation replaces the constant k by an expression involving the coefficients m and n of a hypothetical law of force in which the attraction and repulsion are proportional to terms of the type $1/r^m$ and $1/r^n$ respectively.

The magnitudes involved in equation (1) are such that for most metals Q_0 is of the order 10^4 to 10^5 cal., whilst k is a small number of the order 1 to 3. E_T is of the order 1000 at room temperature, and increases by roughly 600 for each 100° rise of temperature. At low temperatures, the results depend essentially on E_T and Q_0 , but at high temperatures the terms kE_T becomes increasingly important.

The question of the validity of equation (1) has involved a great deal of confusion, and some of the main causes of difficulty may be summarized as follows :

(a) The term Q_0 may be determined by several methods which are referred to in § 5 below. Some of these are at the best only approximations, whilst others involve physical constants which may only be known approximately. This means that errors of the order 5 to 20% may be introduced at the outset, through an incorrect choice of Q_0 .

(b) The fact that the theoretical basis of Grüneisen's relation involves the assumption of a single Debye characteristic temperature has led to a general tendency to calculate E_T by means of Debye functions. This has led to confusion in two ways. In the first place, specific heats do not always follow Debye functions accurately, and in some cases there is a tendency to choose the value of Θ so that it gives the correct specific heat at the low temperatures, where the variation in C_v is most interesting. For the calculation of changes of volume, however, it is much more important for the specific heat to be correct at high temperatures, because at low temperatures both C_v and α are small, and relatively large errors may occur without much effect on the change in volume. In the second place, the uncertainty in the value of Q_0 is not always realized. A procedure sometimes adopted is to deduce Q_0 by one of the approximate relations given below, and to obtain a value which is in error by a few per cent. When the value of Q_0 is combined with the correct* value of Θ , the calculated changes in volume are naturally wrong by an amount corresponding with the error in Q_0 . Instead of this being recognized, a fictitious characteristic temperature Θ' is then introduced, and is used to calculate a fictitious value of E_T which gives a better agreement with the volume changes. In fact it is hardly unfair to say that an incorrect value of Q_0 is made an excuse for introducing a fictitious Θ' , and then the combination of the two is claimed as a proof of the correctness of Grüneisen's relation. It is clear that, logically, this is very unsatisfactory, whilst for the purposes of the practical use of Grüneisen's relation it is of course valueless, since the fictitious Θ' can be deduced only when the changes in volume are known. It is this which makes the otherwise interesting work of Nix and MacNair (1941) useless for the present purpose. These authors show convincingly that for some metals the coefficients of expansion agree with equation (1), provided that Q_0 is chosen arbitrarily, and that E_T is calculated from the Debye function with a suitably chosen value of Θ . It was, however, sometimes necessary to make slight adjustments to the values of Θ obtained from specific-heat data, and consequently, although the conclusions were of considerable interest, they did not constitute a proof of the relation between changes of volume, and the real value of $E_T = \int_0^T C_v dT$.

(c) Apart from the above points, there has been a tendency to confuse the issue by considering not the actual changes in volume, but the calculated and observed mean coefficients of expansion over relatively wide ranges of temperature. It may, for example, at first appear satisfactory to state that the calculated and observed mean coefficients of linear expansion are 2.0×10^{-5} and 2.2×10^{-5} respectively, but the difference is equivalent to a 10% error in changes of length and a 30% error in changes of volume.

If we ignore the theoretical implications of Grüneisen's relation, and consider it solely from the practical point of view, it will be seen that there are two questions to be decided. It is necessary to examine first of all whether changes in volume are related to E_T by a relation of the type of equation (1), provided that Q_0 and k are chosen suitably, and secondly, to see how Q_0 and k are to be

* We are here assuming that the substance is one to which a Debye function applies accurately.

determined, the correct choice of Q_0 being the real essential. In §§ 4 and 5 we shall examine these two points.

§ 3. ACCURACY OF EXPERIMENTAL DATA

For critical examination of equation (1) it is necessary to consider the accuracy of the experimental work on thermal expansion, and it is convenient to consider first the work on isotropic (cubic) structures. Measurements of the coefficients of expansion of massive metal at high temperatures are often unreliable owing to the effects of gas or other impurities in the metal. Thus, variations in the thermal expansion of copper have been ascribed to dissolved hydrogen acting on traces of oxide with the liberation of steam, which, on blowing out of the metal, may produce an abnormal expansion. These difficulties are overcome by the use of high-temperature x-ray technique, which enables the true lattice spacings to be measured, irrespective of the presence of blowholes. Lattice-spacing measurements at room temperatures should be consistent to 1 part in 50,000, but the high-temperature work involves many possible errors (e.g. calibration of thermo-couples, differences in temperature during exposure, etc.), and the accuracy is undoubtedly lower. Thus Wilson (1942), in repeating very careful work on the lattice spacings of aluminium, found differences of the order 1 part in 14,000. It seems probable, therefore, that even in good quality work on simple substances, giving satisfactory high angle x-ray reflections, the lattice-spacing measurements may sometimes contain errors increasing from 1 part in 20,000 at moderate temperatures to 1 part in 10,000 or 1 part in 5000 at high temperatures.

With non-cubic substances, the coefficient of expansion generally varies with the direction relative to the crystal axes. Measurements on massive polycrystalline rods are often valueless, because of preferred orientation of the crystals.* This difficulty can be overcome by measuring the expansion of a cube in three directions, but such measurements are uncommon. Measurements on massive single crystals should be satisfactory, but some of the early work in this connexion is very inaccurate, presumably owing to accidental strain of the crystals. It is also necessary to distinguish carefully between investigations designed expressly to measure coefficients of expansion and those in which data on expansion were obtained as a by-product of other work (e.g. of compressibility). In the latter type of work the experimental arrangements may be unsuitable for accurate measurements of expansion. The x-ray method is again satisfactory, but since it involves the determination of two parameters, the error is at least twice as great as for cubic substances, unless the structure is such that a high-angle line of the form $(h, 0, 0)$ enables one parameter to be obtained independently of the choice of axial ratio.

For temperatures below 0°C. there does not yet seem to be an x-ray camera designed for detailed work over a range of temperatures, but fortunately there is accurate work on polycrystalline specimens of the cubic metals referred to below, and on single crystals of the non-cubic metals.

We shall not discuss in detail the accuracy of specific-heat data. For some

* Bars of drawn and annealed metal nearly always show marked preferred orientation, whilst cast bars may show some preferred orientation.

of the metals dealt with below, the specific heats at room temperatures are probably reliable to 1 part in 300, but for many metals the data are uncertain by at least 1%. At low temperatures the accuracy is less, but as the specific heats are smaller, the effect is not serious for the calculation of changes in volume. At high temperatures there is a serious falling off in the accuracy with which specific heats are known, and it is seldom that results are reliable above 500° or 600° c.

§ 4. THE ACCURACY OF GRÜNEISEN'S EQUATION (1)

In order to examine the accuracy of equation (1) it is necessary to calculate E_T . For the present purpose it seemed better to discard Debye functions entirely, since their use serves only to introduce the additional complication of the correct choice of Θ . The policy adopted has been to use the actual experimental values of C_p , and to determine the value of $\int_0^T C_v dT$ by graphical integration. The accuracy of the integration is fully as great as is justified by the errors in C_p . The value of $(C_p - C_v)$ can be obtained from the relation (see W. Nernst and F. A. Lindemann, 1911)

$$C_p - C_v = C_p^2 T A,$$

where T is the absolute temperature, and the constant A is given by the relation

$$A = \frac{(3\alpha)^2 V}{\chi C_p^2},$$

α being the linear coefficient of expansion, V the atomic volume, and χ the compressibility. To a first approximation A can be assumed to be independent of temperature, and since at the lower temperatures $(C_p - C_v)$ is small, errors in A are important only at the higher temperatures. The assumption of a constant value of A at the higher temperatures may legitimately be criticized, but on the one hand it does not seem justifiable to examine this point further until the specific heats are known to a higher degree of accuracy, and, on the other, the method used has the advantage of simplicity, and gives the values of E_T in a straightforward way from the C_p data.

The values of k in equation (1) have been taken from the *Handbuch d. Physik*, vol. 10, and as the term kE_T is relatively small at low temperatures, errors in the assumed values of k affect the results only at the higher temperatures.

It is convenient to separate the results for cubic and non-cubic metals. Examination suggested that the data were known accurately for the metals detailed below. References to the original sources are given in the Appendix, where the accuracy of some of the results is also discussed.

Cubic metals. Tables 1, 2, 3, 4 show the results obtained for silver, copper aluminium and iron. In these, and later tables, the quantity calculated is the volume, Ω , per atom in (crystal angstroms)³. Ω is thus equal to one-quarter the volume of the unit cell of the face-centred cubic structure, and one-half the volume of the unit cell of the body-centred cube. In all cases the observed value of the lattice spacing at room temperature is taken as the starting point, and from this the value of Ω at room temperature is deduced, and is used to calculate Ω_0 in equation (1). The values of Ω at different temperatures are then calculated, and are compared with the observed values. At low temperatures,

these "observed values" are based on the coefficients of expansion of massive metal, and at high temperatures the results of accurate measurements of lattice spacings are used. In the case of iron, however, there is no accurate high-temperature x-ray work, and the "observed" values of Ω have been calculated from the coefficients of expansion, which are fortunately known accurately for this metal.

The figures in table 1 show that for silver the observed and calculated values of Ω are in excellent agreement over the whole range 20 to 973° K. Between 20 and 90° K. the calculated increase in Ω is 0.031 Å³ as compared with the

Table 1. Silver

Temperature (° K.)	Volume per atom (Å ³) calculated	Volume per atom (Å ³) observed
973	17.725	17.718
773	17.469	17.468
572	17.237	17.241
273	16.929 value assumed	16.929
171	16.837	16.838
90	16.773	16.773
20	16.742	16.739

$Q=108,010.$ $k=3.07.$

Table 2. Copper

Temperature (° K.)	Volume per atom (Å ³) calculated	Volume per atom (Å ³) observed
1044	12.260	12.257
944	12.179	12.183
773	12.053	12.054
573	11.903	11.909
273	11.726 assumed	11.726
172.5	11.670	11.672
87.5	11.632	11.635
20	11.621	11.623

$Q=117,000.$ $k=2.63.$

observed value of 0.034 Å³. The difference is equivalent to an error of roughly 10% in $\Delta\Omega$, and hence of about 3% in the coefficient of linear expansion, and this is probably within the experimental accuracy at these low temperatures, where the changes in volume are very small. The results of table 1 suggest that Grüneisen's equation (1) is quantitatively exact over a range of 1000° K. to within the limits of accuracy now available.

Table 2 shows the data for copper, but for the present purpose this metal is not so satisfactory as silver, because the thermal expansion of massive metal in the range 0 to 500° C. does not agree exactly with the expansion of the lattice as measured by x-ray methods. As will be seen from table 2, Grüneisen's equation

is in fairly satisfactory agreement with the data over the range 20 to 1044° K. There are slight differences on opposite sides of 273° K. which cannot be allowed for by changing the value of Q_0 , and these are the result of the above-mentioned discrepancy between the results of the two methods of measuring the thermal expansion. If the expansion above 0°C. had been calculated from the data for massive bars of copper (see Appendix) a slightly different value of Q_0 would

Table 3. Aluminium

Temperature (° K.)	Volume per atom (A. ³) calculated	Volume per atom (A. ³) observed
773	17.149	17.163
673	16.997	17.000
573	16.854	16.852
473	16.719	16.714
373	16.592	16.590
273	16.4744 assumed	16.4744
193	16.391	16.391
83	16.306	16.305
20	16.293	16.290

$$Q=84,110. \quad k=2.84.$$

Table 4. Iron

Temperature (° K.)	Volume per atom (A. ³) calculated	Volume per atom (A. ³) observed
958	12.098	12.066
876	12.033	12.019
774	11.963	11.958
678	11.903	11.902
577.5	11.845	11.845
478	11.793	11.792
376	11.745	11.744
293	11.709 assumed	11.709
225	11.682(3)	11.682(5)
131	11.652	11.653
91.5	11.643	11.643
73	11.640	11.640
20	11.638	11.638

$$Q=171,000. \quad k=2.27.$$

have given a better agreement over the range 0 to 553° K., at the expense of a worse agreement at higher temperatures. It does not, however, seem justifiable to discuss the figure in further detail until the causes of the differences between lattice expansion and bulk expansion are understood.

The figures in table 3 show that, for aluminium, equation (1) is confirmed fairly satisfactorily from 20 to 673° K., but at 773° K. the observed expansion is greater than the calculated value by an amount which should exceed the

experimental error, and it seems probable that genuine deviations from equation (1) set in at from two-thirds to three-quarters of the temperature of the melting point on the absolute scale. At 473° K., there is a difference of 0.005 Å² between the calculated and observed values of Ω . This is equivalent to 1 part in 10,000 in the measurement of the lattice spacing, and this is probably somewhat greater than the experimental error, since the work of Wilson (1942) (see Appendix) was carried out in great detail in this range. The specific heats are, however, only known to two significant figures over most of the temperature range, and it can hardly be said that the above difference is outside the experimental error. As in the case of silver, the assumed value of Q_0 gives slightly too small a change in volume between the two lowest temperatures. A small difference in the assumed value of Q_0 would give a better agreement in the range 0 to 273° K., at the expense of a slightly worse agreement at higher temperatures, but it does not seem profitable to discuss this until the coefficients of expansion at low temperatures, and the specific heats at all temperatures, are known more accurately.

Table 4 shows the results for iron, and this metal is of particular interest, because its specific heat cannot be explained in terms of a single Debye characteristic temperature. It will be seen that, in spite of this, there is an extremely good agreement * between the calculated and observed values of Ω in the range 20 to 774° K. This suggests that equation (1) does not depend on the assumption of a single Debye characteristic temperature, and that the failure of equation (1) for other metals at high temperatures is the result of an effect other than a divergence of the specific heat from a simple Debye function. In the case of iron it will be seen that at temperatures above 774° K. the calculated values of Ω are larger than those observed, and although the difference is not very great † at 958° K., it suggests that the destruction of the ferro-magnetism involves energy changes which are not related to changes in volume by means of equation (1).

Non-cubic metals. Table 5 shows the calculated and observed values of Ω for magnesium, which crystallizes in the close-packed hexagonal structure with an axial ratio ($c/a = 1.62354$) not very different from that for close-packed spheres ($c/a = 1.6330$). The agreement between the calculated and observed values is clearly not so good as for the cubic metals. From 20 to 473° K. the differences are within the experimental error,‡ and the difference only becomes really pronounced above 773° K., where the observed expansion is clearly greater; the behaviour here resembles that for aluminium. In the range of temperature below 673° K. there is a suggestion of a systematic departure from equation (1) which could not be corrected by adjusting the value of Q_0 , but the differences are of the same order as the experimental accuracy, and more reliable values for the coefficients of expansion of single crystals at low temperatures and of the specific heats are clearly desirable before discussing the matter further.

* It is to be emphasized that the interest here is that equation (1) holds not merely where a fictitious characteristic temperature is used to calculate a fictitious E_T , but also when the real value of E_T is inserted.

† Reference should be made to the Appendix for difficulties in estimating the specific heats of iron.

‡ The coefficient of expansion of magnesium is so high that in the range 273 to 373° K. an error of 1° changes Ω by approximately 0.002. An error of 0.01 in Ω is equivalent to one part in 2300 in the volume, or one part in 7000 in the lattice spacings. Since two parameters have to be determined, this is hardly outside the experimental error.

Table 6 shows the results for zinc, which is of interest as a highly anisotropic metal,* which at very low temperatures shows a negative coefficient of expansion perpendicular to the hexagonal axis. In this case equation (1) fails at the lowest temperatures. There is a fair agreement with equation (1) over the range 133 to 573° K., but a critical test is, unfortunately, not possible. The data for high temperatures are from the lattice-spacing measurements of Owen and

Table 5. Magnesium

Temperature (° K.)	Volume per atom (A ³) calculated	Volume per atom (A ³) observed
873	24.349	24.379
773	24.099	24.094
673	23.864	23.847
573	23.643	23.630
473	23.434	23.437
373	23.238	23.246
273	23.0561 assumed	23.0561
193	22.923	22.924
90	22.787	22.790
20	22.754	22.753

$Q=77,660.$ $k=2.18.$

Table 6. Zinc

Temperature (° K.)	Volume per atom (A ³) calculated	Volume per atom (A ³) observed
623	15.602	{ 15.580 15.586
573	15.519	{ 15.502 15.508
473	15.365	{ 15.358 15.364
373	15.221	{ 15.217 15.223
273	15.0861 assumed	15.0861
173	14.959	14.954
133	14.914	14.905
93	14.875	14.860
20	14.833	14.813

$Q_0=70,750.$ $k=2.68.$

Yates (1934) (see Appendix), whose value for Ω_{273} is 15.080 as compared with what seems to be the more accurate value of 15.0861 of Jette and Foote (1935). If the difference between the two values is due to a constant factor such as the calibration of a camera, then the values of Owen and Yates require correction by 0.006 to make them comparable with the value assumed (15.0861) for calculation in table 6. If, on the other hand, the difference is due to an error in one

* The structure is close-packed hexagonal with axial ratio $c/a=1.8563$ (Jette and Foote, 1935) at 25° C.

individual experiment of Owen and Yates, the remaining figures of these investigators should be left unaltered. It is for this reason that two values are given at each temperature above 273° K. in table 6, and it is clearly unjustifiable to discuss the results in greater detail until the data are more certain.

From tables 1 to 6 we may conclude that, except for the magnetic transformation in iron, the data for the cubic metals are in very good agreement with equation (1) up to a temperature of the order $\frac{2}{3}$ to $\frac{3}{4}$ of the melting point on the absolute scale. For the non-cubic metals, the equation fails at very low temperatures if the substance has a negative coefficient of expansion in one direction, but is otherwise fairly satisfactory until a temperature of the order $\frac{2}{3}$ of the absolute melting point is reached, although the accuracy of the data is not yet sufficient for a critical test.

§ 5. THE CHOICE OF THE CONSTANT Q_0

From the preceding sections it will be appreciated that the correct choice of Q_0 is all-important if Grüneisen's equation is to give accurate results. The usual relation given in this connexion is

$$Q_0 = \frac{V_0}{\gamma \chi_0}, \quad \dots \dots (2)$$

where γ is the constant referred to in § 1, and equals $-V \frac{\partial V}{\partial T} / C_v \frac{\partial V}{\partial p}$. This method is extremely unsatisfactory because it makes Q_0 inversely proportional to γ , and the values of γ are often very uncertain. Apart from this, the value of χ_0 , the compressibility at the absolute zero, is usually uncertain by several per cent, and it is not surprising that the values of Q_0 obtained in this way require a fictitious characteristic temperature before they are in agreement with the changes in volume.

An alternative method, given by Simon and Vohsen (1928), is to write

$$Q_0 = \frac{C_p}{3\alpha} + 2kE_T, \quad \dots \dots (3)$$

where C_p and α are the values of the specific heat and coefficient of expansion at room temperature. This relation is obtained, as an approximation only, by writing equation (1) in differential form. In principle, the method is much more satisfactory than that involving equation (2), since the term $2kE_T$ (where $k = \gamma + \frac{2}{3}$) is now only a relatively small correction to the value of $C_p/3\alpha$, and the uncertainty in the value of Q_0 is much less serious. Unfortunately, although justified for the purpose of Simon and Vohsen, the approximation is unjustified for high accuracy at room temperature, and it can readily be shown that the values of Q_0 obtained from equation (3) depend on the purely arbitrary value of the temperature (20° C.) at which C_p , α and E_T are taken, even though the substance is one which obeys equation (1).

It will be seen that both of the relations (2) and (3)* require a knowledge of α at some temperature. Consideration will show that if a value of α is known, we can determine Q_0 directly from equation (1) without any approximation. This can be done either by writing equation (1) in differential form, and solving

* γ involves α through the term $\partial V/\partial T$.

the equation for Q_0 , or alternatively by simple methods of trial and error. We have found the latter procedure more convenient, as it provides the constants required for later calculations, and it is convenient for computation. If, for example, the value of α is known at 273° K. , we may assume a reasonable value of Q_0 , and use this to calculate Ω_{253} and Ω_{293} and then adjust Q_0 until the expansion between 253° K. and 293° K. agrees with the known coefficient of expansion at 273° K.

This method is simple and straightforward, and in cases where the expansion obeys equation (1), the method gives correct values of Q_0 , subject only to the errors in the assumed values of α . This uncertainty must not be minimized, because there are many substances for which the coefficients of expansion are uncertain by a few per cent. The direct method of obtaining Q_0 is, however, much more satisfactory than those based on equations (2) or (3), because these involve not only the uncertainty in α , but also other approximations or quantities which are liable to considerable error.

If the substance dealt with is one to which equation (1) applies only approximately over a restricted range of temperatures, then the value of Q_0 obtained by the direct method will be the best possible value for use in the ranges of temperature adjacent to that at which α is known, and will thus be the best value for extending the value of α to new temperatures. We suggest, therefore, that this direct method of obtaining Q_0 is the correct procedure to use. Having obtained the value of Q_0 which gives the correct value of α at the known temperature, it is, of course, of great theoretical interest to see whether this value agrees with equation (2), but the use of equation (2) to obtain Q_0 appears undesirable.

§ 6. ANOMALOUS THERMAL EFFECTS

The principal danger in using Grüneisen's relation for calculating changes in volume is that anomalous thermal effects may occur which are not related to volume changes by means of equation (1). In some cases (e.g. ammonium chloride, germanium) definite peaks appear on the temperature/specific heat curves, and these can readily be detected. If, however, the effect is less pronounced, the specific-heat curve may appear normal, and the abnormality can only be detected when the expansion is studied. At present the experimental evidence on this point is confusing. In the case of lithium, the work of Simon and Bergmann (1930) suggests that the expansion and specific heats in the range 95 to 273° K. do not obey equation (1), although the expansion data would satisfy this equation if a fictitious characteristic temperature were assumed. The differences involved are not very great, and would be covered by errors of the order 5% in the mean coefficients of linear expansion. Further work appears desirable, since the method used was one in which a rod of metal 30 cm. long was stood vertically in a copper tube. At temperatures above 0° C. the metal was so soft as to undergo deformation, and it is not certain whether the observed coefficients of expansion refer to partly strained material. It is also to be noted that the data of Simon and Bergmann for lithium were accompanied by results for copper which it was suggested showed the same effect, although this was not confirmed by the work of Adensstedt (1936), whilst the detailed work described above suggests strongly that in the range -253 to 0° C. the

thermal expansion and specific heat agree excellently with Grüneisen's equation. It appears, therefore, that much further work is required before these suggested small anomalies can be regarded as established.*

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APPENDIX

Notes on the experimental data

Silver. The lattice spacings above 273° K. were taken by linear interpolation between the two adjacent values given by Hume-Rothery and Reynolds (1938), whose work extended over the range 18 to 943° c. These values agree with measurements of other workers on massive silver. The coefficients of expansion at low temperatures are taken from Landolt's Tables (Ergänzungsband II), and are based on the work of Keesom and Jansen (1927). The specific heats are from Landolt's Tables (Ergänzungsband III), which give specially selected values of C_p and C_v .

Copper. The lattice spacings above 273° K. are from the work of Hume-Rothery and Andrews (1942). At temperatures from 87·5 to 273° K., the most accurate expansion data appear to be those of Nix and MacNair (1941), whose results are in excellent agreement with those given in Landolt's Tables (Ergänzungsband II). Nix and MacNair also give data for massive copper at high temperatures, and these are not in exact agreement with the lattice-spacing data of Hume-Rothery and Andrews. The difference is particularly marked at 573° K., where the measured lattice spacing is 3·6259(5) Å., whilst that calculated from Nix and MacNair's data would be 3·6254. If Nix and MacNair's data were used throughout, a slightly different value of Q_0 would give a better agreement with Grüneisen's relation over the range 0 to 573° K., at the expense of a slightly worse agreement at higher temperatures, but at present it seems that the expansion of massive copper at high temperatures varies from one sample to another, and we have thought it best to use the lattice-spacing data. The thermal expansion in the range -253 to -185° c. is taken from the data in Landolt's Tables (Ergänzungsband II). The different volumes of Landolt's Tables give specific-heat data from many sources, whilst Dockerty (1937) gives detailed tables of C_p and C_v from 28 to 194° K. There is good agreement between

* It must be emphasized that no real conclusion can be drawn from the mere fact that a specific heat/temperature curve can be represented as the sum of a Debye curve, and a correction term which reaches a maximum at some temperature. All Debye curves give a zero specific heat at $T=0$, and the same specific heat at very high temperatures. It follows, therefore, that a true Debye curve can always be represented as the sum of a curve for an appropriate value of Θ and a correction term which reaches a maximum in some range. The correction term must be of the correct magnitude before its existence can be used as an indication of an anomalous effect, and it is seldom that the specific heats are known with sufficient accuracy. As pointed out by Simon and Bergmann, further work down to the temperature of liquid hydrogen is required before the phenomenon is fully understood.

the results of different investigators below room temperature. At high temperatures the data of Jaeger, Rosenbohm, and Bottema (1933) have been confirmed by Carpenter and Bryant (1939).

Aluminium. The coefficients of expansion at low temperatures are from the work of Ebert (1928), and the lattice spacings at high temperatures are due to Wilson (1942). As in the case of copper, the expansion of the lattice and of massive metal are not in exact agreement at high temperatures. The specific heats are taken from different volumes of Landolt's Tables.

Iron. Nix and MacNair (1941) investigated the expansion of massive metal in great detail over the range -181.5 to $+700^{\circ}\text{C}$., whilst Ebert's work extends to -253°C . The specific heats at low temperatures were measured by Simon and Swain (1935). Above room temperature the position is very obscure. Several investigators have claimed that the specific heat of iron shows fluctuations, and G. Naeser (1935) gives a specific heat temperature curve with a series of small peaks and valleys, although these were not found by H. Klinkhardt (1927); both investigators used very pure metals. For the present purpose we have used a smooth curve based on the results of Klinkhardt and Baerlecken. If a toothed curve really exists, it will not greatly affect the calculations, because some parts will lie above and some below the smooth curve, and on integration the positive and negative areas will tend to cancel.

Magnesium. The lattice spacings at high temperatures are from the work of Hume-Rothery and Raynor (1939), whose data for the range 0 to 200°C . are in good agreement with the work of Goens and Schmid (1936), who measured the coefficients of expansion of large single crystals. The work of the latter investigators extended down to -253°C ., and their results have been accepted below 0°C . For the specific heats the data of Seekamp (1931) and of Williams, Eastman and Young (1924) are in good agreement.

Zinc. The lattice spacings at high temperatures are from the work of Owen and Yates (1934), whilst the thermal expansion of single crystals at low temperatures was investigated by Grüneisen and Goens (1924). The two investigators overlap in the region 0 to 100°C ., and are not in exact agreement. For the specific heats, the results of different investigators as given in the different volumes of Landolt's Tables enable a satisfactory curve to be drawn up to 100°C ., but there is a difference of opinion as to whether abnormal effects exist between 100 and 200°C . and between 330 and 340°C . Jaeger and Poppema (1936) give the mean values of C_p between 0°C . and higher temperatures, and we have based our calculations above 100°C . on their figures, which include any anomalous specific-heat effects.

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ILLUMINANTS FOR COLORIMETRY AND THE COLOURS OF TOTAL RADIATORS

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ABSTRACT. The colours of total radiators are discussed and methods of estimating the colour-temperature to be assigned to a colour not on the locus of the colours of total radiators are outlined. The filter method of calibrating tungsten lamps at the National Physical Laboratory is given, with an indication of the probable accuracy of the calibration.

The history and properties are given for the three standard illuminants A, B and C recommended for colorimetry by the Commission Internationale de l'Eclairage in 1931. Other illuminants, such as the equal-energy illuminant E, are mentioned, and the colours of them are compared with those of daylight.

§ 1. INTRODUCTION

THIS lecture deals first with the colours of total radiators and the estimation of the colour-temperature that is to be given to a colour that is not exactly on the locus of the colours of total radiators. Then we consider the standard illuminants A, B and C that are used for colorimetry, what they are, how they are established, and how permanent they are likely to be. After this, an account of other illuminants that have been proposed will be given, together with indications as to how their colours compare with those of daylight.

To begin, definitions of the terms that will be used frequently might be helpful.

Firstly, what is the spectral distribution of energy from a total radiator? A theoretical investigation shows that this spectral distribution of energy of a total radiator is given by Planck's formula,

$$E_{\lambda\theta} d\lambda = C_1 \lambda^{-5} [\exp(C_2/\lambda\theta) - 1]^{-1} d\lambda,$$

where $E_{\lambda\theta} d\lambda$ is the energy between the wave-lengths $\lambda \pm d\lambda/2$ for a radiator at θ° K. and C_1 and C_2 are constants. It is generally agreed that experimental results are in accordance with those given by this formula (Brown, 1941; Committee on Colorimetry, 1944).

The value recently given for C_2 (Birge, 1941), the only constant that concerns us here, is 1.4384 ± 0.0003 , cm. deg. The values suggested for C_2 have varied considerably. 1.4320 was accepted for the international temperature scale in 1927 (*Travaux et Mémoires*, 1927), 1.4360 was considered for this scale in 1939 (Comité International des Poids et Mesures, 1939), 1.4350 has been used

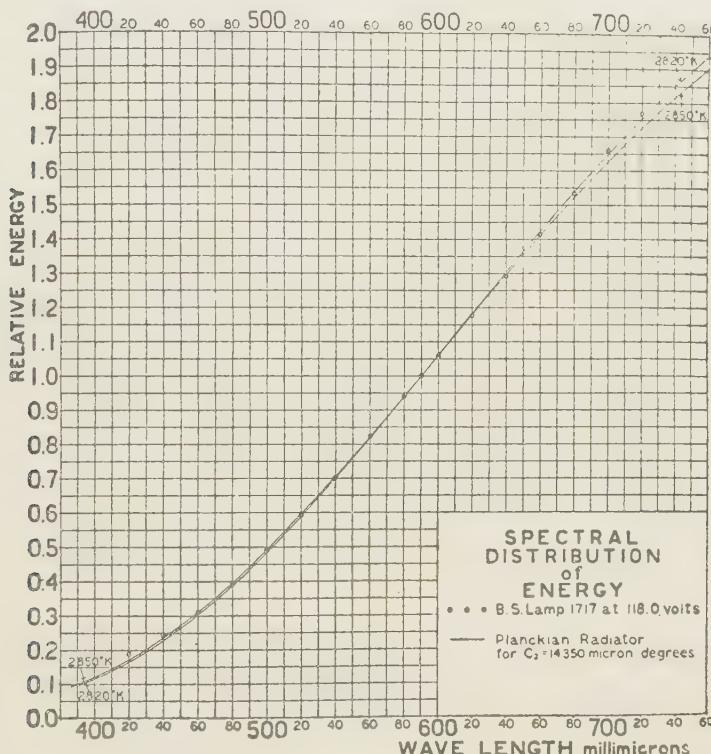


Figure 1. Spectral distribution of energy, B.S. Lamp No. 1717 and Planckian radiator at 2820° and 2850° K.

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extensively for colorimetry since 1931 (Smith and Guild, 1931-2), and no doubt a value higher than 1.4360 will be accepted internationally in the future.

Secondly, what is the spectral distribution of energy from a tungsten-filament lamp over the visible range of the spectrum? Measurements by Coblenz and calculations by Priest show that it is very similar to the distribution calculated from Planck's formula if colour-temperature is substituted for temperature. A graph from Priest's paper (Priest, 1922) is reproduced as figure 1.

Throughout this paper the relative spectral distributions of energy of total radiators and tungsten-filament lamps, for visible radiation, are derived from Planck's formula, and C_2 has the value 1.4350 which was suggested by the Commission Internationale de l'Eclairage, 1931 (Smith and Guild, 1931-2) for the

calculation of the spectral distribution of energy of the C.I.E. standard illuminant A.

Thirdly, what is the colour-temperature of a tungsten-filament lamp? By this we mean the temperature of the total radiator which is estimated to have the same colour as the lamp. The international temperature scale (*Travaux et Memoires*, 1927), which has been used since 1927, is based on the melting point of gold (1336° K.) and Wien's radiation law with a value 1.432 cm. degrees for C_2 .

§ 2. THE COLOURS OF TOTAL RADIATORS

With these definitions in mind, the colours of total radiators will first be considered. We have found at the National Physical Laboratory that the trichromatic coefficients of the colours of total radiators are often wanted to five-figure accuracy over a large colour-temperature range. Since it takes three or four hours to calculate the colour of a radiator directly from Planck's formula, it was considered worth while to produce tables of the trichromatic coefficients of the colours on the C.I.E. system, so that the colour of any radiator, at any temperature between 1500 and 9000° K., could be obtained by linear interpolation in a few seconds. In addition, if the tables were smooth to six figures, they could be the basis for other tables that would be required if the value for C_2 were altered or if the colours were to be expressed against the micro-reciprocal degree scale (Priest, 1933), which will be explained later.

Tables were prepared in 1940–1 with a value 1.4350 for C_2 . The energies were calculated from Planck's formula at approximately 500° K. intervals for the temperature range 1500 – $11\,000^{\circ}$ K., then the colours were calculated from these energy values using the *Condensed Tables for Colour Computation* (Smith, 1934). The trichromatic coefficients so obtained were interpolated for the range 1500 – $10\,900^{\circ}$ K. The use of Smith's tables about halved the work involved, since the full tables for colour calculations as recommended by the C.I.E. have entries at seventy-nine wave-lengths and Smith's tables entries at only forty wave-lengths. If only half the entries of the C.I.E. tables, that is at 0.38 – 0.01 – 0.77μ , had been used to calculate the colours from the spectral-energy distributions, errors of 0.0001 to 0.0002 in the trichromatic coefficients would have been expected, whilst with the condensed tables the errors should not exceed 0.00001 .

When in 1941 Birge suggested a value 1.4384_8 for C_2 , the tables were revised to refer to this value by reading from the 1.4350 tables the trichromatic coefficients for the temperatures $\theta_{1.4350} \times 1.4350 \times (1.43848)^{-1}$ over the range 1500 – 100 – 9000° K., then interpolating these values to tenths. These tables have been published (Harding, 1944 a). The validity of this procedure can be seen if the value C_2/θ of Planck's formula is considered. If the value of C_2 is changed, the locus of the colours of total radiators will not be altered on the colour chart, but the temperature corresponding to a particular colour on the locus will alter. For example, if $C_2 = 1.43848$ and $\theta = 2000^{\circ}$ K., then $C_2/\theta = 1.43848/2000$. If C_2 had been taken as 1.4350 , the temperature given to the radiator having the same colour would be $2000 \times (1.4350) \times (1.43848)^{-1} = 1995.2^{\circ}$ K., because $C_2/\theta = 1.43848/2000 = 1.4350/2000 \times (1.4350) \times (1.43848)^{-1}$.

The locus of the colours of the radiators is shown in figure 2, where it is

interesting to note that the locus can be represented very closely by a parabola. A better parabola than the one indicated can probably be found, but since the actual temperatures cannot be located on the curve, the only value that the formula has is to serve as a guide to the shape of the curve on the colour chart. The "mired" or micro-reciprocal-degree scale is marked on the locus, and it can be seen that the mired scale is more evenly spaced than the colour-temperature

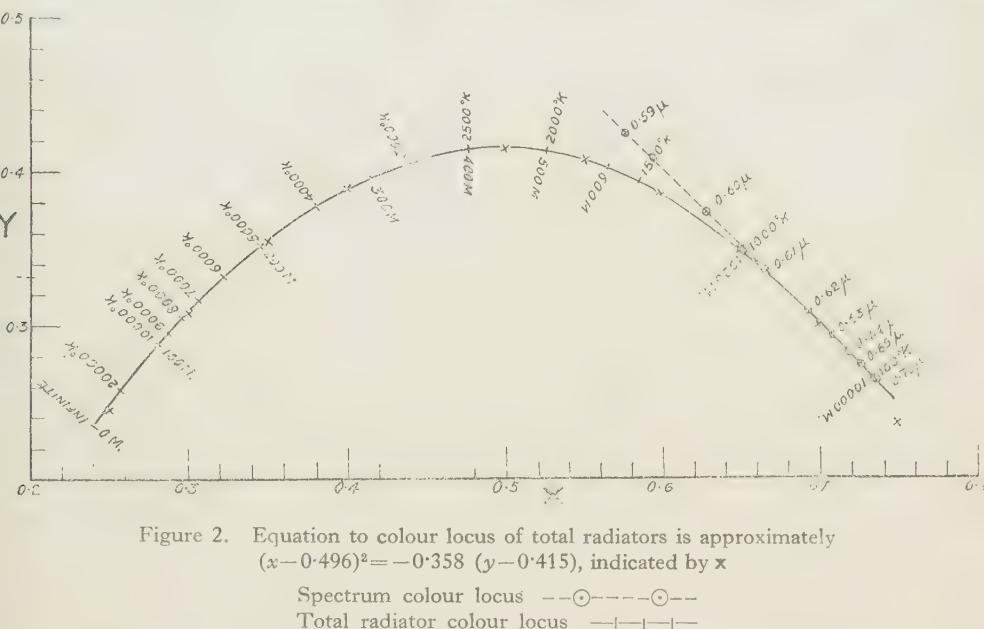


Figure 2. Equation to colour locus of total radiators is approximately $(x - 0.496)^2 = -0.358(y - 0.415)$, indicated by x

Spectrum colour locus ---○---○---
 Total radiator colour locus ---|---|---

scale over the range of temperatures from about 2000° K. to infinite temperature. A mired is a million divided by the colour-temperature in °K., and serves a useful purpose in colour-temperature calculations since the use of it generally avoids calculating reciprocals. Tables giving the trichromatic coefficients for total radiators for the mired range 0–1–660 mireds ($C_2 = 1.43848$) have been prepared at the Laboratory also.

§3. COLOURS NOT ON LOCUS FOR TOTAL RADIATORS

The next problem is that of the colour-temperature to be given to a colour which is not on the locus of the colours of total radiators, and an example will explain why this is so important.

Suppose that a filter is being used for colour-temperature measurements, and that this filter is placed in front of a standard lamp in order to colour-match it with another lamp at a different colour-temperature. It may not be possible to get the photometer fields to be exactly the same colour by altering the lamp voltages because, owing to the properties of the filter, one photometer field is always slightly, but perceptibly, greener than the other. When different observers make colour-matches under these conditions, it is most likely that their settings will not agree, and that one observer would be quite sure, on looking at the photometer fields, that he would never make the setting that another observer would make. When this sort of thing happens, the general procedure

is to take the mean reading of a number of observers, but since a few preliminary measurements will most likely explain the disagreement and avoid observer differences in the final result, they are well worth some consideration.

The mechanism of colour-matching may be illustrated by figure 3. If two lamps L_1 and L_2 are colour-matched at a temperature θ represented by the point P on the locus of the colours of total radiators RS, then a very pale green filter is put in front of L_2 , so that the colour of L_1 is represented by P and that of L_2 by C, an observer will see the colours represented by P and C. To try to restore the colour-match the colour-temperature of L_1 may be altered to correspond to the point B (L_1, θ_1) on the locus RS. The observer can then

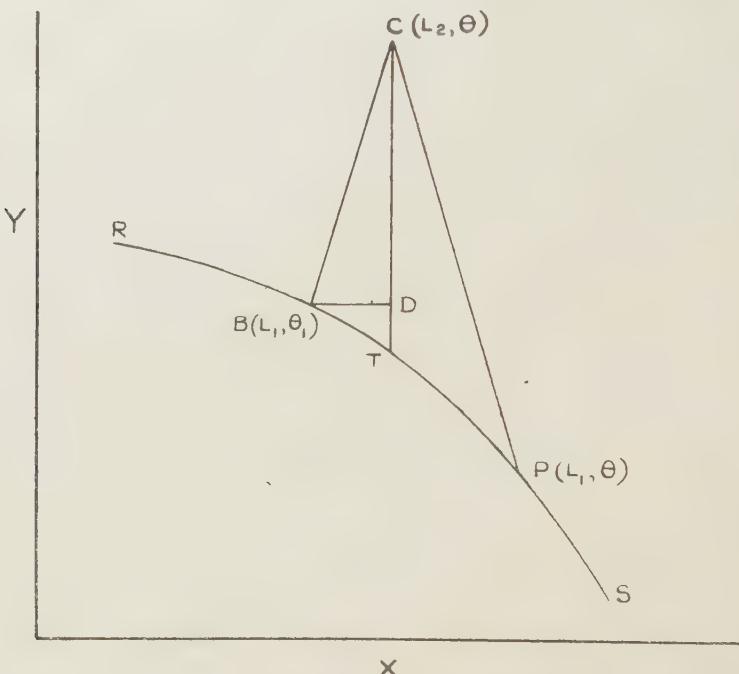


Figure 3. Colour-temperature estimation for colours not on the locus of the colours of total radiators.

be said to estimate colours off the locus with those on the locus along the line CB. If CD is drawn through C parallel to the Y-axis to meet a line through B parallel to the X-axis at D, and to meet the locus at T, the angle DCB can be conveniently defined by giving the value of BD if $CD = 0.001$.

The greenness of the off-locus colour C with respect to the locus RS can be expressed by the value of CT, which is subsequently called Δy . Δy is the difference between the Y-coefficient of the colour represented by C and the Y-coefficient of the colour of the total radiator which has the same X-coefficient. If $\Delta y = 0.001$ and the two colours are viewed with a Lummer-Brodhun photometer having a ten-degree field, there will be an observable colour difference between the two parts of the field, one field always appearing slightly greener than the other however carefully the colour-temperatures of the lamps are adjusted to try to get a colour-match.

About 1930, when the R, G and B system of expressing colours was used at the National Physical Laboratory, the method used to fix the line CB was to divide the red coefficient of the off-locus colour by the blue coefficient, then to find the colour of the total radiator which had the same red to blue ratio. The reason for adopting this method was that experiments by Guild and Young indicated that it gave the correct answer provided that a predetermined method of colour-matching was used.

A second method by Judd (Judd, 1936 a), which was based on the Uniform Chromaticity Chart, is much sounder and will be mentioned later.

This problem of the slope of the line CB arose at the National Physical Laboratory when we were measuring the colour-temperatures of lamps with a blue liquid and a yellow glass filter. The results of the colour-temperature measurements using the alternative filters differed by the easily measurable amount of 10°K ., and it seemed that the most probable explanation of the disagreement was that the colour-temperatures assigned to off-locus colours were incorrect.

Donaldson, of the National Physical Laboratory, determined the way in which several observers estimated the nearest colour-temperature which corresponded to a given off-locus colour. He first colour-matched two lamps at a given colour-temperature using a Lummer-Brodhun photometer with a ten-degree field, then inserted a pale green filter (Δy equal to approximately 0.001) in front of one of the lamps and altered the colour-temperature of the other lamp until the best colour-match setting that could be obtained was found. The slope of CB was then found from a knowledge of the colour of the filter, which had been determined spectrophotometrically, and the calibration of the colour-temperatures of the lamps against their voltages. The results of these measurements are shown in figure 4, where the results obtained by the red to blue (or X to Z of the more recent C.I.E. system) ratio method used by Guild and the Judd method are included for comparison purposes. The letters near to each curve identify the observer.

It is seen from this diagram that if $\Delta y = 0.001$, a value which gives a just-perceptible green colour difference, two observers may differ in their settings by about 12°K . at 2500°K ., and a larger difference than this is likely to be expected for most single-component filters which are available for colour-temperature measurements. If, however, the filters have been carefully prepared, Δy need not exceed 0.00004 (Harding, 1944 b), so that observer differences, due to colour differences alone, should not exceed 0.5°K .

Owing to the large variations of individual observers in their estimations of the nearest colour-temperature that corresponds to an off-locus colour, we have made it a practice to use the observer's own estimation of the slope of BC, as given in figure 4, whenever the value of Δy is large enough to cause errors exceeding a degree.

To sum up, there are two factors governing the problem of the colour-temperature that shall be given to a colour. Firstly, if the colour is on the locus of the colours of total radiators, then it is only the value which is given to C_2 in Planck's formula to calculate the colours of the total radiators that matters; that is, illuminant A may be expressed as 2848°K . ($C_2 = 1.4350$), or 2842°K . ($C_2 = 1.4320$),

because $C_2/\theta = 1.4350/2848 = 1.4320/2842$. Secondly, if the colour is not on the locus of the colours of total radiators, but is near to it, say Δy not greater than 0.010, there is the additional complication that the value of the colour-temperature estimated by various observers will be different and the characteristics of individual observers will have to be considered.

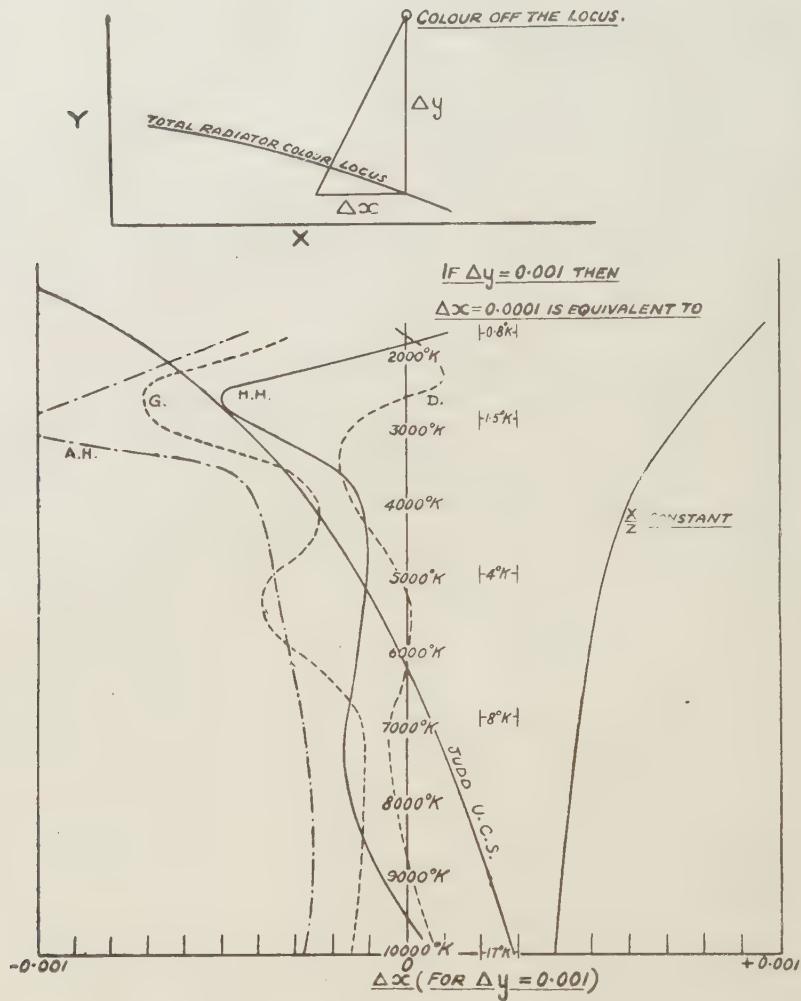


Figure 4. Colour-temperature estimation for colours not on the locus of the colours of total radiators.

When estimations of this kind are made subsequently, it will be assumed that $C_2 = 1.4350$ and that angle DCB is defined by the measurements made by a particular observer at the laboratory.

§ 4. THE STANDARD ILLUMINANTS

We can now go on to the consideration of the first illuminant for colorimetry, standard illuminant A, which is defined by the C.I.E. as "A gas-filled lamp operated at a colour-temperature of 2848°K." "The spectral distribution of

energy from this source may be taken for all colorimetric purposes to be that of a black-body at a temperature of 2848°K . The value assumed for Planck's constant C_2 is 14350 micron degrees " (Smith and Guild, 1931-2).

The value 2848°K . for the colour-temperature of the lamp comes from the United States of America and originated thus: as long ago as 1917, Coblenz of the Bureau of Standards measured the spectral distribution of energy of a five-hundred-watt gas-filled tungsten lamp designated as B.S. Lamp No. 1717, operated at 118.0 volts (Priest, 1922). Priest calculated the colour-temperature of this lamp from the spectral distribution of energy in the following way. The values of the products of the visibility function and the spectral distribution of energy of the lamp, and also the products of the visibility function and the spectral distributions of energy of various Planckian radiators, were plotted as ordinates and wave-lengths as abscissae. A value λ_c was calculated for each of these curves, λ_c being the wave-length coordinate of the centre of gravity of a thin template of uniform density bounded by the wave-length axis and the curve.

Priest found that λ_c for the lamp was the same as that for a Planckian (total) radiator at 2848°K ., with an uncertainty of less than 5°K .

A five-hundred-watt lamp was then calibrated against the lamp B.S.1717, and this was sent to the Nela Laboratory. Its colour-temperature, determined by colour-matching with a total radiator, was given by Forsythe in a letter to Priest as 2848°K . (Priest, 1922).

Priest concluded from the good agreement obtained between the colour-temperature derived from Coblenz's isothermal measurements and that measured at the Nela Laboratory by colour-matching with a total radiator, that instead of referring to a particular lamp as a reference standard, a satisfactory standard source would be one closely approximating to the Planckian spectral distribution in the visible spectrum and having a colour-temperature of 2848°K .

This same history for standard illuminant A is also outlined by Wensel, Judd and Roeser (1934), who say that the exactness of the agreement of Priest's and Forsythe's results was apparently accidental and has created the impression that this 2848°K . point on the colour-temperature scale was determined with far more accuracy than was actually the case.

There are two points worth mentioning here. Priest's calculations were made about 1921, which was before the 1924 C.I.E. values for the visibility function and the 1931 C.I.E. trichromatic data were available. It is unlikely that the visibility function that we now use would have affected his results, but it certainly would be interesting to calculate the colour of the lamp from Coblenz's spectral-energy values, using the C.I.E. trichromatic data, to see if the same colour-temperature value of 2848°K . would be obtained.

The calibration of a lamp at 2848°K . is the next problem. By definition a lamp will be operating at 2848°K . if it colour-matches a total radiator which is at a temperature of 2848°K . At the National Physical Laboratory we do not maintain a total radiator in continuous use for routine colour-temperature measurements, but rely on sets of six, sixty-watt, hundred-volt, tungsten vacuum lamps which have been calibrated against a total radiator at several temperatures and for which voltage values have been interpolated at 10°K . intervals over the range $1800\text{--}2400^{\circ}\text{K}$.

By direct colour-matching, using a ten-degree field Lummer-Brodhun photometer with contrast strips, and taking the mean of eight readings obtained by making two observations for each of the four possible positions of the photometer head, lamps are calibrated from 1800–2400° K. By means of a blue liquid filter (Guild, 1925-6) which is placed in front of the lamp operating at the lower colour-temperature, or a yellow glass filter (Harding, 1944 b) in front of the lamp at the higher colour-temperature, the range of the vacuum lamps can be extended to 3000° K., which is about the maximum colour-temperature at which lamps are operated for long periods as standards. To reach the highest colour-temperatures attainable with tungsten-filament lamps, 3644° K. (Priest, 1922), gas-filled projector lamps are calibrated by the filter method against the vacuum standards, then these projector lamps are again used with the filter.

A filter required for these measurements has to be carefully designed. There is only sufficient time here to mention that it must be permanent, very little affected by temperature change, and must give good colour and energy matches between tungsten lamps for the whole range over which standardized lamps might be required. For some purposes a yellow filter is to be preferred, and for others a blue one. Since the best energy and colour matching that we have so

Table 1

Lamp voltage (volts)	Colour temperature (° K.)		
	N.B.S.	N.P.L.	Difference
34.5	2046	2039	7
44.3	2239	2234	5
51.1	2360	2351	9
75.2	2727	2715	12

far been able to get has been with a yellow filter, and since it is an advantage to put the filter in front of the brighter lamp, we often prefer to use a yellow filter.

Before leaving the problems of colour-temperature measurement, it might be worth mentioning what has probably been obvious almost from the beginning of this paper, that is, that a colour-temperature can only be given to a lamp if it exactly colour-matches a total radiator. If the lamp bulbs are slightly coloured, or if the energy from the lamp is not approximately Planckian, then difficulties arise. The colour-temperature scale, however, serves a very useful purpose in defining the operating properties of lamps, and our experience with the filter that we use and the lamps that we have calibrated has been that colour-matches have generally been so good that the observer has not been prepared to say that they are not perfect.

The accuracy of the value of the colour-temperature that is given to a lamp can now be considered. A comparison of measurements made both by the National Bureau of Standards and the National Physical Laboratory in 1934 on a projector lamp are given in table 1.

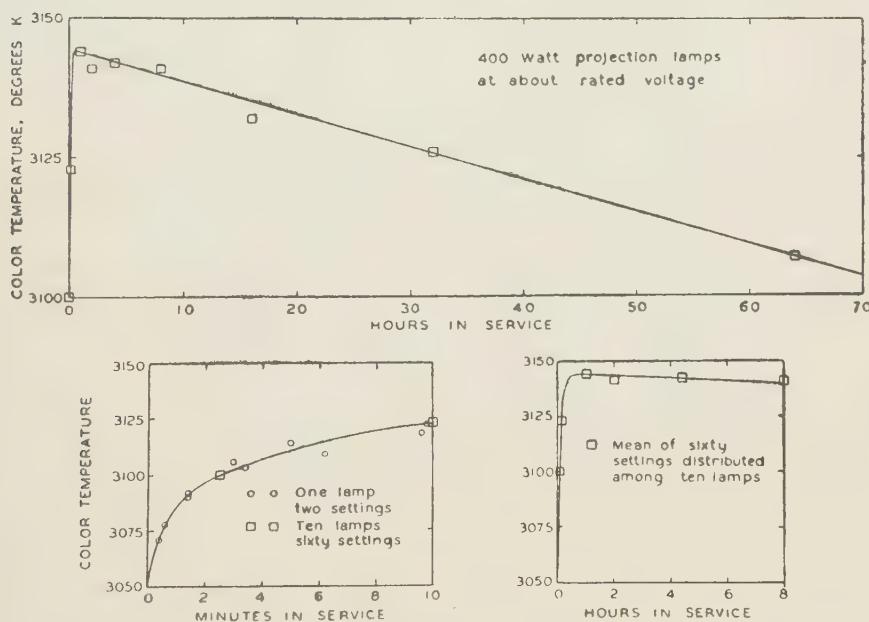
The colour-temperature of a lamp measured with or without a filter can generally be repeated to one or two degrees. Calibrations made with a blue

liquid filter and a yellow glass filter over the range 1950–2848° K. gave results in agreement to 2° K. (Harding, 1944 b).

Next comes the permanency of the calibrations of lamps which are probably similar to those that we use in this country, namely, projector lamps for standard illuminant A and vacuum lamps for colour-temperature standards. The

Table 2

Lamp type	Colour-temperature (° K.)	$\frac{d\theta}{dt}$ (° K./hr.)
Projection	3140	-0.6 ± 0.1
	2850	-0.06 ± 0.01
	2360	-0.006 ± 0.005
Commercial vacuum	2360	-0.01 ± 0.08
Standard vacuum	2360	-0.05 ± 0.04



Colours of sunlight and daylight.

Figure 5. Colour temperature of unseasoned lamps as a function of time in service.

The colour temperature rises rapidly during seasoning, then declines slowly.

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general behaviour of new projector lamps (Judd, 1936 b) is shown in table 2 and figure 5, both taken from Judd's paper.

The other two standard illuminants for colorimetry are obtained by using liquid filters with standard illuminant A.

Liquid filters were used at the National Physical Laboratory before the C.I.E. 1931 recommendations were made. About 1924 Guild required a

"standard white" illuminant for his measurements of the spectrum colours: these measurements, together with those of Wright, were eventually to form the basis for the 1931 C.I.E. colorimetric system. R. H. Sinden (1923) mentioned a filter which had been developed by Pfund and which, when used with a suitable illuminant, reproduced very closely the spectral distribution of energy

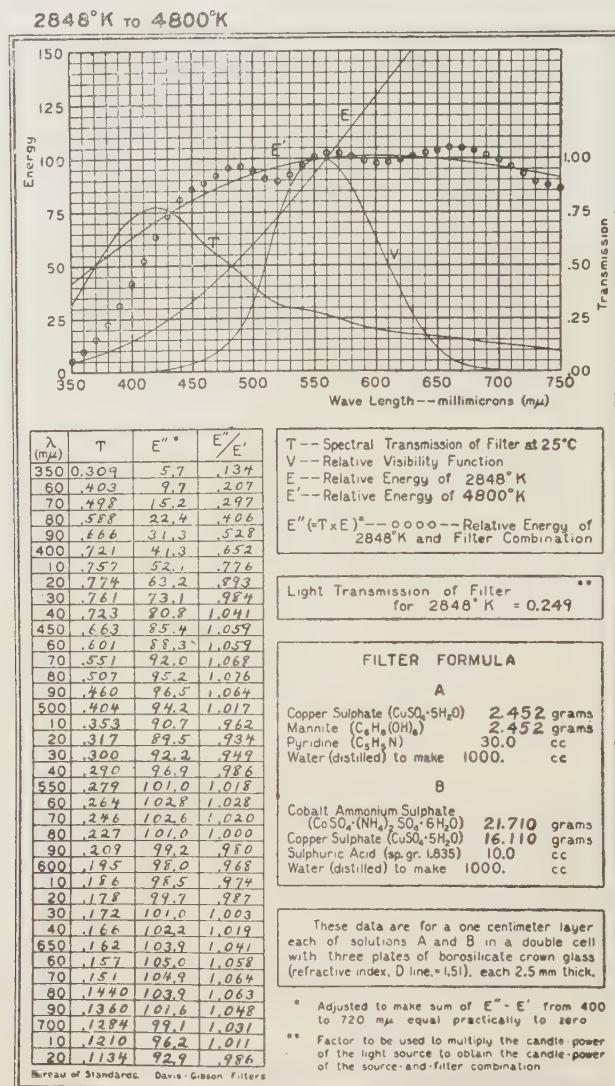


Figure 6.

in sunlight. This filter consisted of a double-compartment cell. One compartment contained an ammoniacal solution of copper sulphate and the other an aqueous solution of the sulphates of copper and cobalt. Guild wrote to Pfund for information about this filter and received a reply stating that Pfund had not yet completed his investigations, so that no information as to the compositions of the solutions was available. Guild's colleague Young therefore

investigated the filters *ab initio* and two filters were developed. One was to raise the colour-temperature of a lamp at 2360° K. to about 2900° K. in order to calibrate a lamp at 2900° K. using the vacuum standards. The other was designed to raise the colour-temperature of a lamp at 2900° K. to about 4800° K. to give a standard "white light" (Guild, 1930-1; Davis and Gibson, 1931 a). These solutions were used at the National Physical Laboratory up to 1931, when the colorimetric specifications were revised, and the C.I.E. recommended the use of a Davis-Gibson filter in conjunction with standard illuminant A (Smith and Guild, 1931-2). The filter chosen was one which had a colour almost the same as that of the N.P.L. white-light filter (Davis and Gibson, 1931 a), so that measurements made before 1931 would still be of value. The description of the filter for standard illuminant B, which with standard illuminant A is

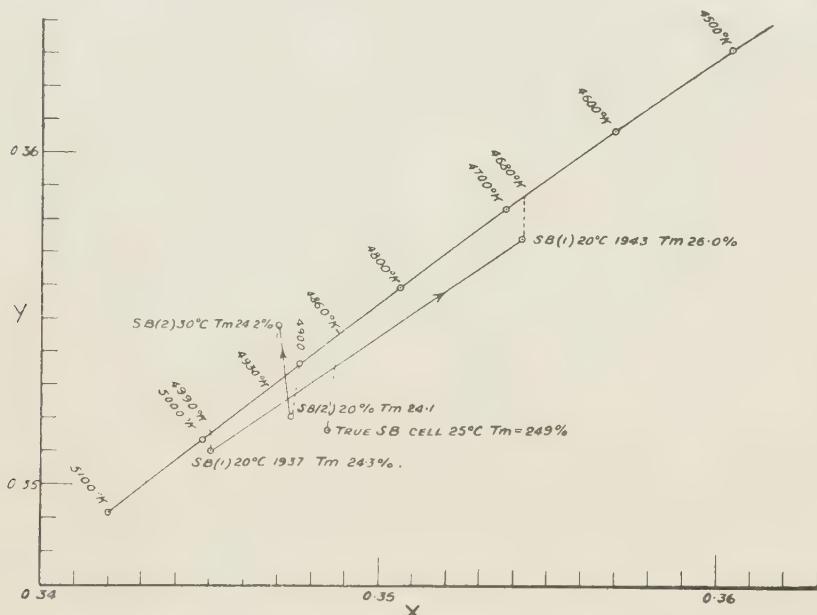


Figure 7. Colours of illuminant B filters for a 2848° K. total radiator as an illuminant.

intended to represent the yellower phases of daylight, is given in figure 6, which is the reproduction of a chart obtained from Davis and Gibson's publication which has just been referred to. The colour of the filter with standard illuminant A as an illuminant is

$$0.34842X + 0.35161Y + 0.29997Z \quad (\text{Smith and Guild, 1931-2}),$$

the transmission as given by the chart is 24.9 % and the colour-temperature corresponding to the colour is 4860° K. Solutions made at the National Physical Laboratory contained in glass cells (Donaldson, 1933) have colours close to the C.I.E. colour and examples are given in figure 7, where the effects of ageing and temperature change are shown.

It can be seen that the colours of freshly prepared filters are slightly greener than the C.I.E. colour, but the differences are small. Considerable care is

necessary in preparing the solutions if filters made at different times are to repeat their colour characteristics. The procedure that has been adopted is to recrystallize the copper sulphate and cobalt ammonium sulphate, which are of A.R. quality; the crystals are then dried and weighed according to the specification.

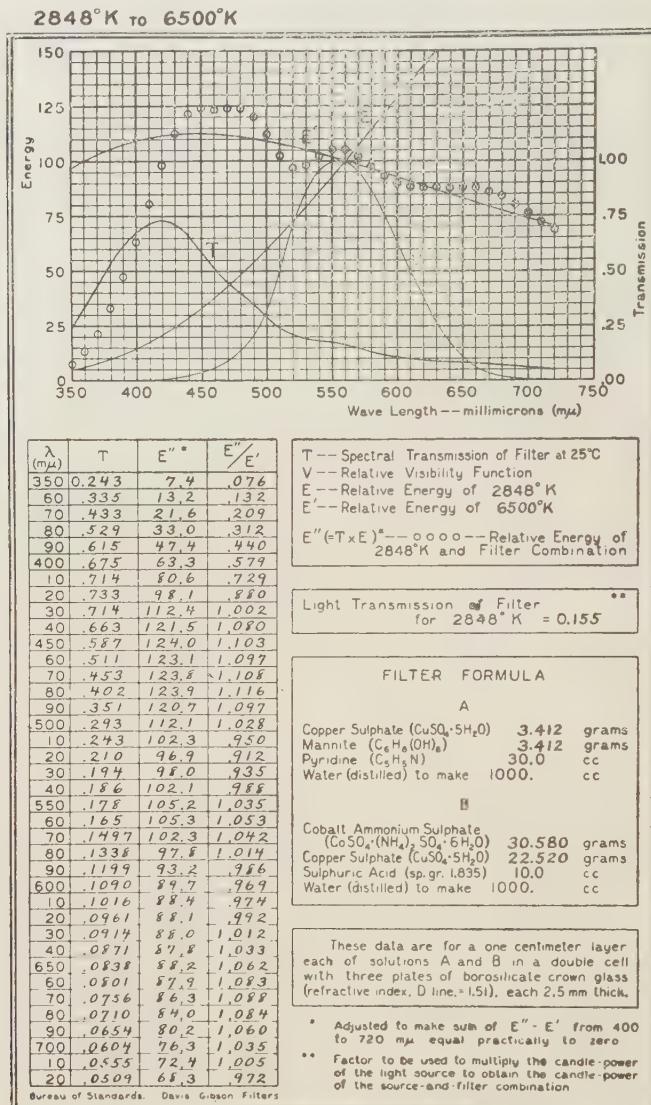


Figure 8.

The next illuminant is standard illuminant C, which is standard illuminant A with another Davis-Gibson filter. The illuminant, which is intended to represent the bluer phases of daylight, has not often been used in this country, and we are not in a position to give any of our measurements on its properties. The chart for the filter for illuminant C as received from Davis and Gibson (Davis and Gibson, 1931 b) is reproduced as figure 8.

The colour of the filter with standard illuminant A is

$$0.31006 X + 0.31616 Y + 0.37378 Z \text{ (Smith and Guild, 1931-2),}$$

and the transmission given by the chart is 15.5 %. The colour-temperature corresponding to the colour is 6660° K.

§ 5. OTHER ILLUMINANTS

An illuminant E was mentioned in the *Proceedings of the International Commission on Illumination*, 1939. This is illuminant A with a Davis-Gibson filter (Davis and Gibson, 1934), and the colour of the illuminant is

$$\frac{1}{3}X + \frac{1}{3}Y + \frac{1}{3}Z.$$

The colour of the lamp and filter combination is too far from the total radiator locus for an equivalent colour-temperature to have much meaning, but a probable value is somewhere between 5250–5450° K. The suggested advantages of this

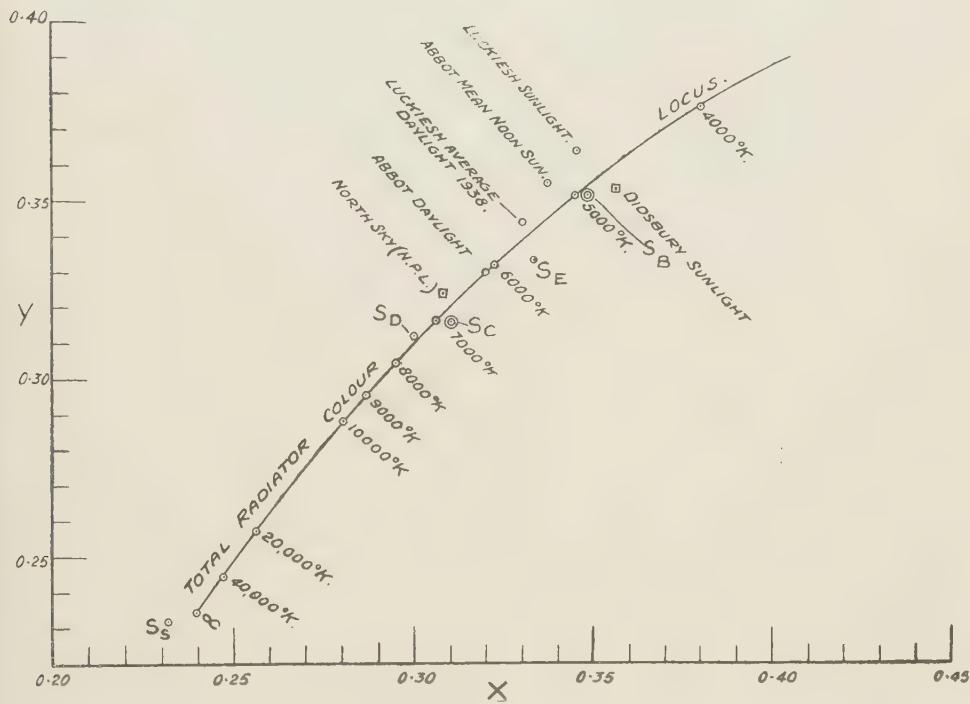


Figure 9.

filter were that it approached daylight more satisfactorily than the standard illuminants B and C, and that many technical and conceptual difficulties could be eliminated by the use of it. These reasons do not seem to be sufficient to justify a change from the illuminants now used, firstly because the colour of the equal-energy illuminant is not closer to the colours of daylight than are the colours of the B and C illuminants, as indicated in figures 9 and 10, and secondly because the technical and conceptual difficulties referred to appear to be of negligible importance.

Illuminants designated D and S (Kelly, Gibson and Nickerson, 1943) have been used in the United States of America. Illuminant D is intended to represent lightly overcast north sky and is stated to have a colour-temperature of 7500° K. It consists of Macbeth (Corning) daylight glass with a lamp at 3000° K. and the colour is given as

$$0.29992X + 0.31201Y + 0.38807Z.$$

This illuminant has been selected for comment because it is made from glass. If melts of glass were reproducible so that the trichromatic coefficients of the colours were reproducible to within 0.001 of a given value, they would be con-

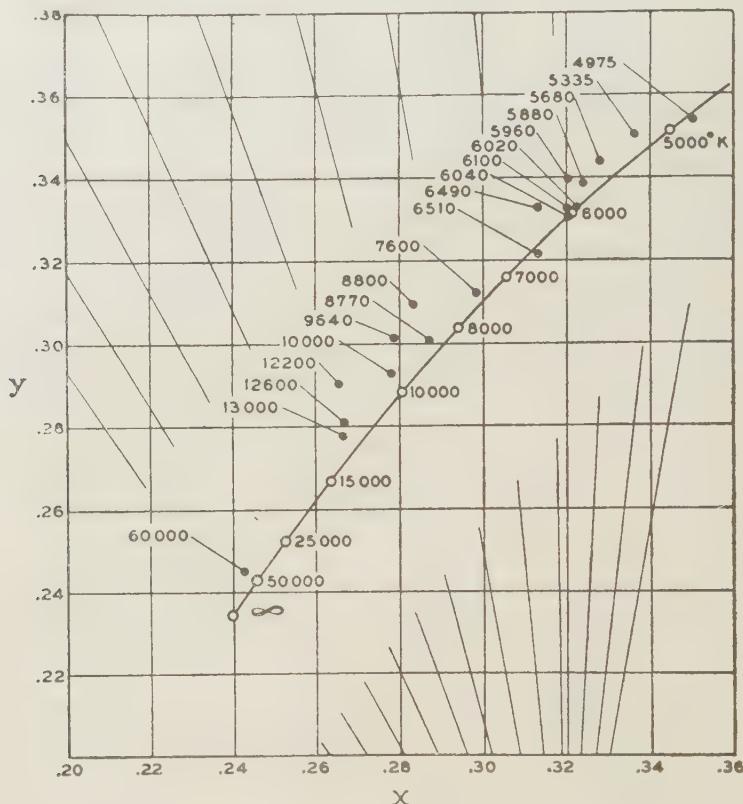


Figure 10. Section of the I.C.I. colorimetry diagram, showing the location of points representing various phases of daylight with respect to the black-body line. The diagonal lines represent various values of "micro-reciprocal degrees" (mireds).

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sidered useful filters to use for standard illuminants. Our experience, however, has shown that melts of glass obtained over a considerable number of years differ appreciably, and for this reason single-component glass filters are unlikely to displace liquid filters until glass manufacturers have improved the repeatability of their melts.

Illuminant S is intended to represent extremely blue sky (Gibson, 1940). The trichromatic coefficients of its colour are

$$0.23194X + 0.23176Y + 0.53630Z.$$

The positions of the colours of these filters on the colour chart are shown in figure 9. In addition are given the colours of daylight measured in the United States of America: Abbot Daylight (Nickerson, 1941), Luckiesh Sunlight and Average Daylight, 1938 (Moon, 1941), Abbot Mean Noon Sun (British Standard Specification No. 793-1938); also the colours of daylight measured in Britain, for Didsbury Sunlight and North Skylight (British Standard Specifications 793-1938 and 950-1941). Other measurements of the colours of daylight (Taylor and Kerr, 1940) are given in figure 10.

§ 6. CONCLUSIONS

To conclude, there are a few remarks on the colours of daylight and the standard illuminants. Taylor (Nickerson, 1941), commenting on the colours of daylight in America, says that at Cleveland the colour-temperature of a clear zenith sky can be $60,000^{\circ}\text{K}.$, a slightly hazy north sky $12,600^{\circ}\text{K}.$, that smoke in the air reduces the colour-temperature still more, and that a completely cloudy or overcast sky gives an energy distribution which corresponds to approximately $6500^{\circ}\text{K}.$ He states that in half an hour the colour-temperature of daylight from a north sky may vary by several thousand degrees. Our experience at the National Physical Laboratory is that the colour-temperature of north skylight has varied from $5000^{\circ}\text{K}.$ to $20,000^{\circ}\text{K}.$ In view of these wide variations in the colours of daylight it is difficult to say which of the illuminants is the most satisfactory.

There is one consideration that should be made when filters are used to reproduce daylight. The bluer the filter the lower is its transmission; for instance, the transmission of the illuminant B filter is about 25 % and that of the illuminant C filter about 16 %, and bluer filters have lower transmissions. For most colorimetric work we require to get as much light of the required quality on the specimen as we can without making it hot. If the filter is put between the lamp and the specimen, it gets hot and its colorimetric properties alter; if the filter is put between the eye and the specimen it is the specimen that gets hot, and this also is not desirable. The transmission of the filter should therefore be as high as possible. This means that the colour-temperature of the radiation transmitted by it should be as low as possible consistent with its colour being in the daylight range. It is probably for this reason that illuminant B has been used so much in this country.

ACKNOWLEDGMENT

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ON THE MEASUREMENT OF THE EFFECTIVE AREA OF A SEARCH COIL

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ABSTRACT. A condenser null-method for the determination of the effective area of a search coil is described. The underlying principle is to compare the area of the unknown coil with a calculable area, the two coils being used alternately in a powerful, constant magnetic field, of which the region of uniform intensity has been extended by the use of pole-pieces with large area. The flux in each coil as it cuts the field can be exactly neutralized by the charge of a condenser. The ratio of the two areas is given as a ratio of two resistances. An accuracy to four significant figures is possible.

§ 1. INTRODUCTION

THE effective area of a small search coil containing a large number of entangled turns, such as is used in measuring magnetic fields which are homogeneous only over small volumes, cannot in general be determined with any degree of accuracy by calculation from the dimensions of the coil. The experimental way of calibrating a search coil (Stone, 1934) is by the use of calculable fields. The coil is placed with its plane at right angles to a field H (oersteds) produced by a standard solenoid carrying a current I (amp.),

and the mutual induction M (henrys) between the two is balanced against an inductometer whose primary is joined in series with the solenoid. The inductometer may be so adjusted that, on reversing the current, the flux in the secondary just balances the flux induced in the search coil. Then the effective area A (cm^2) is evidently given by

$$MI = AH/10^8.$$

A number of intermediate steps may be required in passing from the relatively small fields which are accurately calculable to the large fields which it may be desired to measure.

In 1939, Nettleton and Sugden, in connection with susceptibility determinations, described a method consisting in the measurement of the mutual induction between the search coil and a pair of large Helmholtz coils. If the experiment is then repeated with a coil of known area, the ratio of the two areas will be the same as the ratio of the mutual inductances which are measured by balancing against an inductometer.

Obviously, the accuracy in these methods depends on the certainty with which the mutual inductance can be known, whereas the sensitivity depends on the strength of the uniform magnetic field employed. In general, the fields produced by solenoids or by Helmholtz coils are very small compared with the fields produced by an electromagnet.

We shall describe here a sensitive method involving only the comparison of two resistances.

§ 2. APPARATUS AND PROCEDURE

Quite recently, the authors (1944) described, in a work on magnetic-field measurement, how the flux induced in a search coil can be neutralized by the charge of a condenser. The same principle is applied here. The essential features of the experimental arrangement are shown in the figure.

The conical pole-pieces of an electromagnet are unscrewed and replaced by disks or short cylindrical pole-pieces M , M of large cross-sectional area. In our case the diameter of the core of the electromagnet is 7.5 cm. The diameter of the pole-faces of the disks is 11.5 cm., and the thickness is 1.4 cm.; the air gap is 6.3 cm. With an exciting current of 8 amp., corresponding to a field of 2685 gauss, the induction in a coil of about 300 cm^2 effective area would produce in the reflecting ballistic galvanometer F a deflection of more than 500 mm. for a circuit resistance of about 2000 ohms.

Referring again to the figure, L is a search coil supported on an ebonite frame J carrying a stout wire D dipping into a mercury cup K to a depth of a few cm. (the optimum depth is easily found by trial). B is a battery of about 10 volts and C is a mica condenser of 1 or 2 μF . capacity. F is a fluxmeter or a long-period galvanometer, shunted by a resistance R which includes the resistance of L and the additional resistance R' . P and P' are two large resistance boxes forming a Rayleigh potentiometer. E is a standard cadmium cell connected with a sensitive galvanometer G across a fixed resistance S , and serves to check the constancy of the potentiometer current. The variable resistance X enables a fixed potential difference to be maintained across S .

When the search coil is suddenly raised from the field, the battery circuit is cut off at K. The condenser, being connected to a closed circuit, is thus discharged, the quantity of charge passing through F being

$$\frac{CVR}{R+F} \text{ microcoulombs,}$$

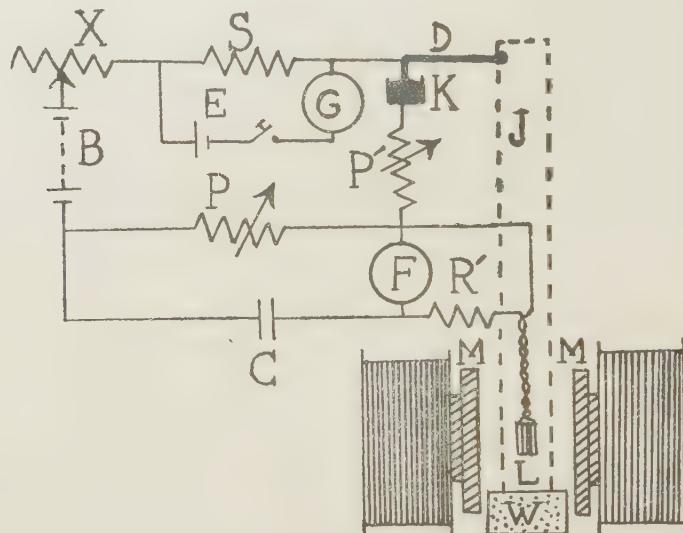
where V is the voltage across P, and F is the resistance of the fluxmeter. Meanwhile, F will receive an opposite impulse

$$\frac{HA}{100(R+F)} \text{ microcoulombs,}$$

due to cutting the field H by the search coil.

Exact compensation can be brought about by adjusting the charging voltage or the shunt resistance or both. When this is achieved,

$$A = 100 \frac{CVR}{H}. \quad \dots \dots (1)$$



Under our experimental conditions, the calculated time of discharge of the condenser to $1/10^4$ of the initial charge through P and the shunted fluxmeter is about 0.1 sec. and is of the same order of magnitude as the time of sudden withdrawal of the search coil manually to a distance (about 20 cm. from the gap) where the field is practically nil. The latter time has been determined in a previous investigation with the aid of an Everett-Edgecumbe time-interval meter arranged in conjunction with two mercury contacts, the first being broken at the instant the motion starts, and the second when a distance of 20 cm. has been traversed.

As the times for the opposite impulses are approximately of the same order of magnitude, and can be made to start together, the two effects on F occur almost in synchronism, since the changes at the ends of these intervals are very small. Thus a sharp balance is possible even with a galvanometer whose period is not too long.

It will be seen from equation (1) that for the same values of H , C and V , the area is proportional to the shunt resistance. In other words,

$$A_2/A_1 = R_2/R_1. \quad \dots \dots (2)$$

With the aid of the standard cell, V can easily be maintained constant to 1 in 10^4 .

By fixing the magnetizing current, and reducing its duration to a few minutes so as to avoid excessive electrical heating of the core, it is possible to keep H constant at least to 1 in 1000.

Again, by employing disk pole-pieces we increase the region of uniform field. In a preliminary experiment with a small exploring coil having a large effective area, it has been found that the field, as measured by the authors' method (*loc. cit.*), is practically uniform, at least up to a radius of 3 cm. from the centre of the gap. Another test of uniformity has been performed by measuring the field with two coils of known area having different linear dimensions.

The two area-coils L_1 and L_2 were constructed on hollow (tubular) ebonite formers turned down to a uniform circular cross-section. Coil L_1 was wound with 36 turns (length 0.9 cm.) of enamelled copper wire of diameter 0.025 cm. on a former of diameter 3.327 cm. The mean radius was thus 1.676 cm. and the effective area of the coil was $A_1 = 317.7 \text{ cm}^2$. Coil L_2 was wound with 56 turns of the same wire on a former of 2.700 cm. diameter. Its length was 1.4 cm. and its area A_2 was 326.5 cm^2 . The windings of the two coils were fixed in position by cellulose dissolved in acetone containing a little ethyl benzoate, the ends bent sharply at right angles and twisted together to reduce their effective area. The coils were then fitted in holes drilled through ebonite frames.

Area measurements were conducted in the following manner. Coil L_1 was held perpendicular to the field and centrally in the gap with the aid of the wax block W . P and P' were then adjusted until the reflecting ballistic galvanometer F showed no deflection on suddenly removing L_1 from the field. Simultaneity of the two impulses could be secured by varying the depth to which the wire D is immersed in the cup K . When exact balance was obtained, the value of the total resistance R_1 shunting F was measured on a good bridge.

Coil L_1 was then replaced by coil L_2 and the experiment repeated. The field current and the potentiometer current were maintained strictly constant, and the previous values of P and C were not changed. Only R_1 was adjusted to R_2 until balance again occurred, and then R_2 was determined.

§ 3. RESULTS

In a typical result, the circuit conditions were:—

$$\begin{array}{lll} B = 12.5 \text{ volts}, & E = 1.0184 \text{ volts}, & V = 5.210 \text{ volts}, \\ S = 1018.4 \text{ ohms}, & P = 5210 \text{ ohms}, & P' = 5900 \text{ ohms}, \\ C = 2.00051 \mu\text{F}. & & \end{array}$$

F was a mirror galvanometer of resistance 881 ohms and period 7.17 sec. A low-resistance galvanometer would have been more suitable, but none was available.

With the area coil L_1 , the shunt resistance $R_1 = 834.0$ ohms.

With the area coil L_2 , the shunt resistance $R_2 = 857.1$ ohms.

Thus,

$$A_2/A_1 = 1.028.$$

By calculation from the dimensions,

$$A_2/A_1 = 1.028.$$

The two results agree to the fourth figure. The agreement may be taken as further indication that the field is homogeneous over a considerable volume.

The unknown search coil L was wound of 100 turns of the same wire as the area coils. It was wound on glass tubing, from which it was afterwards slipped, pressed by thread into a small length and then supported in an ebonite frame. The mean diameter was about 1.26 cm.

With the search coil in the circuit, the shunt resistance satisfying balance under the previous conditions was $R = 348.4$ ohms. The effective area of the search coil L is thus $A = 132.7 \text{ cm}^2$.

§ 4. CONCLUSION

The method here described of comparing areas is very satisfactory, and has the additional advantage that the same arrangement which is used for field measurement is employed again, with the modification that the usual conical pole-pieces of the magnet are replaced by ones with larger faces.

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DISCUSSION

on paper by W. E. BALLARD entitled "The formation of metal-sprayed deposits", *Proc. Phys. Soc.* **57**, 67 (1945).

Dr. G. A. HANKINS. In presenting the paper, Mr. Ballard did not comment on the mechanical or metallurgical properties of the sprayed metal deposits. In using the process for building-up worn shafts, for example, these properties may be important, since it seems to me there is some possibility that under repeated stresses, as in a shaft, a fatigue crack may be started in the built-up layer, and the stress-concentration at the root of the crack might then be sufficient for the crack to be propagated into the original metal of the shaft and result in a fatigue failure.

The fact that the deposit is able to absorb oil appears to be an asset in the case of a built-up journal bearing. Normally, the engineer endeavours to obtain complete fluid-film lubrication between the journal and a bearing ; but in starting or stopping, for example, this oil film breaks down and boundary-lubrication conditions exist. Under these conditions a journal surface which holds a small amount of oil would probably be beneficial.

Mr. F. D. L. NOAKES. I would like to raise three queries with reference to this paper :

(1) As it appears that the chief cause of porosity is the boundary layer of particles, which have solidified before they reach the surface to be sprayed, would it not be possible to reduce, if not entirely to eliminate, the porosity by masking ?

(2) It did not appear quite clear how it is that although a large proportion of the metallic particles are molten when they strike the sprayed surface, and, therefore, may be assumed to be at quite high temperatures, an inflammable material (or a sensitive substance, such as the human hand) is not in any way affected.

(3) All the samples shown and metals quoted would produce sprayed surfaces which, although they may be matte, nevertheless have considerable metallic lustre. For certain processes various components of radio valves, etc., have to be given an optical black finish. Is there any material which can be sprayed which will produce a surface of this nature?

Mr. L. T. MINCHIN. The real mystery of this process to me is the fact that these minute particles of molten metal escape oxidation. Can Mr. Ballard explain this?

AUTHOR's reply. In reply to Dr. G. A. Hankins, the paper as presented was solely written with the idea of presenting some theoretical aspects of metal spraying, and, therefore, was not expanded to cover the practical engineering view-point of the process. I have dealt with this in a paper which was presented to the Institution of Automobile Engineers in January 1942, which dealt rather fully with the question of building up crank-shafts. Many thousands of crank-shafts have been treated by the process and have been found to be entirely satisfactory under most arduous conditions.

It is of course possible that a crack started in the built-up layer might cause the crack to be propagated into the original metal, but after a long experience the author has seen only one case of such a failure, and this was in the case of a crank-shaft which had been subjected to a most rigorous engine test with the object of testing to destruction. In commercial practice, as I have said, there has been no such experience, although the possibility cannot be ruled out. The success of this method of reclamation is undoubtedly due to the absorption of oil within the porous steel deposit and the maintenance of an oil film.

In reply to the first question from Mr. F. D. L. Noakes, I feel that, while it would be possible to avoid a good deal of porosity by masking of marginal particles, it is not a possibility in commercial practice. The losses would be so great in proportion that the process would become uneconomic.

With regard to the second question, the particles are extremely small and they are surrounded by a very large volume of gas which is cold compared with the temperature of the particles themselves; therefore the heat transference from the particle is extremely rapid, and this is the reason why sensitive articles may be sprayed. It should, however, be quickly pointed out that while it is possible to spray thin films of cellophane without scorching, it is necessary in such cases either to move the pistol extremely rapidly or to move the cellophane very rapidly; alternatively, the nozzle distance can be increased beyond the usual economic limits. While it is possible to pass one's hand through the spray at working distance, it would not be possible to hold one's hand still in the spray for any appreciable time. The process is considered cold only because of the rapid transference of heat, not because it is really cold.

Finally, in answer to the third question, there is no metal which gives an optical black finish without some form of after-treatment. Iron alloys, nickel chrome and lead give the darkest coatings, and these are dull grey. It would appear therefore that metal spraying is not a solution to this difficulty.

In reply to Mr. L. T. Minchin, it is quite possible to spray the metal magnesium from magnesium wire without undue oxidation. It appears that only two explanations are possible, and one only seems to be of real importance: this is that the speed of the process is so great that the hot particles are not in contact with the hot oxidizing atmosphere long enough to allow of considerable oxidation. The second factor, which may possibly operate in some cases, is that each particle may be covered with a very thin oxide film which serves to protect the particle from further oxidation.

OBITUARY NOTICES

SIR ARTHUR EDDINGTON, O.M., F.R.S.

"LET us now praise famous men". But when the source of fame is untimely stopped, praise comes less readily from our lips than lamentation from our hearts. And less compellingly: it is no accident that our great personal elegies—*Lycidas*, *Adonais*, *In Memoriam*—commemorate those whose renown was unfulfilled. Of Arthur Stanley Eddington it may truly be said that he is dead ere his prime, and hath not left his peer. For though his years were by ordinary standards not few, and his achievements among the greatest which his time can show, yet so vast was the problem towards which his mind instinctively directed itself that the close of 40 years of uninterrupted labours found him still on the hither side of the climax of his thought. We can see none fitted to carry his work to its completion.

Eddington was born on 28 December 1882 at Kendal, of Quaker parentage. He was thus by birth as well as conviction a member of the Society of Friends, and retained throughout his life the essential humility and equilibrium of spirit fostered by the mode of worship of that Society. His early education at Weston-super-Mare was followed by a course and degree in physics at Owens College, Manchester, after which he proceeded to Trinity College, Cambridge, and became Senior Wrangler in 1904. From 1906 to 1913 he was Chief Assistant at the Royal Observatory, Greenwich, where an early inclination towards the major problems of science became definitely oriented; henceforth astronomy was to provide the medium through which he could explore the universal principles belonging to the "nature of the physical world". His first researches, apart from certain routine work (which, however, he never despised, and to the direction of which he gave due attention throughout his life), were concerned with the large-scale movements of the stars, and his work in this field gave such manifest evidence of his quality that in 1913 he was appointed to succeed Sir George Darwin as Plumian Professor of Astronomy and Experimental Philosophy at Cambridge, and in the following year to the additional post of Director of the University Observatory. Here, with his sister, he resided for the remainder of his life.

Eddington's first book, *Stellar Movements and the Structure of the Universe*, was published in 1914. Though the universe there adumbrated is a very modest affair compared with that which it is now usual to imagine, the book remains a classic, both as a masterly summary of the knowledge of the time in this important subject, and as the first intimation to the world in general of the advent of a fresh and powerful mind, master equally of large conceptions and their embodiment in felicitous and intelligible prose. It has a peculiar interest for me because, knowing nothing of the subject, never having heard of the author, and attracted solely by the title, I acquired a copy, found its general meaning within my understanding, and thenceforward saw the sky with new eyes. In *Stellar Movements* appeared those very expressive diagrams which became known somewhat disrespectfully, but not inaptly, as "rabbits", which I believe he was the first to introduce, in which the characteristics of star-streaming appeared in unmistakable form.

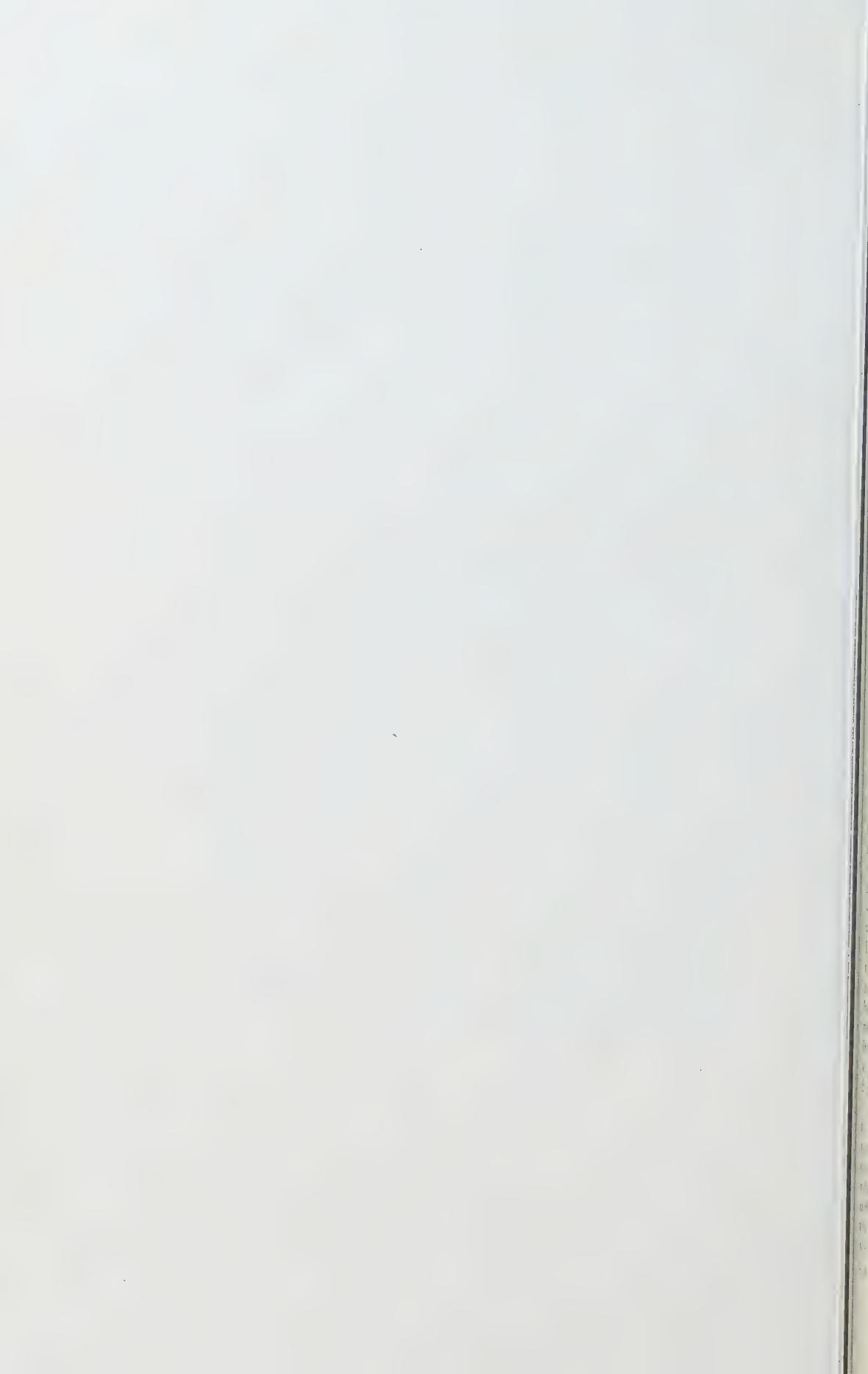
It was appropriate that he should sum up his work on stellar movements at this time, for his thoughts were soon to be occupied by two very different and even more fundamental subjects. One of these was indigenous, the natural product of the fertilization by contemplation of the stars of a mind steeped in physical theory. The physical conditions inside a star had been the subject of a few isolated researches, but nothing of obvious significance had been achieved. Eddington, therefore, virtually created a new branch of astronomy when, in 1916, he published his first paper on the equilibrium of stellar matter. The most conspicuous of the new ideas which he introduced was that radiation rather than convection was the chief agent in transferring energy from the interior to the surface of a star, and that radiation pressure played an important part in supporting the weight of the outer layers. From this it followed that the maximum possible mass of a single material body was, in fact, very close to the greatest known stellar mass, and



A. S. Eddington

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1882-1945

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that so long as a star behaved as a perfect gas, its mass and luminosity should stand in a definite relation to one another.

At that time (up to 1924) it was generally believed that giant stars were virtually perfect gases, and that the transition, through contraction, to the imperfect or "liquid" state coincided with the change to the dwarf condition ; this was, in fact, the essence of Russell's theory of stellar evolution. Much to his surprise, however, Eddington found that the mass-luminosity relation was obeyed not only by giant but also by dwarf stars—indicating either that his theory was fundamentally wrong or that dwarf stars also were perfect gases. Eddington took the second view, justifying his choice by the consideration that, at the temperatures existing inside the stars, the atoms would be so far stripped of their electrons as to allow abnormally high densities, relatively to which the densities of ordinary dwarf stars were so low that they were effectively perfect gases. The argument was clinched by the existence of "white dwarfs", in which, as Eddington and Russell had previously pointed out, the densities appeared to be impossibly high. The impossible, now become actual, not only proved Eddington to be correct (further confirmation was shortly afterwards provided by the Einstein displacement of the white-dwarf spectrum lines), but also showed the necessity for a completely new theory of stellar evolution.

While the germ of this great idea was beginning to evolve naturally in Eddington's mind, there came from outside a disturbing influence of such magnitude that only the most stable intellect could have preserved itself from confusion. The first account of Einstein's general theory of relativity appeared in 1915, but owing to the war it was not until late in 1916 that, through a series of papers by de Sitter in the *Monthly Notices* of the Royal Astronomical Society, it came to the notice of English scientists. It is, I think, one of the most striking evidences of Eddington's mental power that not merely did he protect the development of his work on stellar interiors from interruption by his inevitably strong reaction to this profound conception, but, grasping the essence and implications of relativity with almost incredible speed, he became at once the leading (for some time the only) English exponent of a theory which, to most of his contemporaries, was so recondite as almost completely to elude apprehension. Nor did he merely hold the mirror up to Einstein. The light of relativity was not reflected in his diffusion of it, but absorbed and re-emitted in characteristic radiations (forbidden radiations, some might consider, but that is an open question). Those who, after a quarter of a century of continuous meditation on the subject, feel that at last they appreciate its general significance have only to turn to Eddington's *Report on the Relativity Theory of Gravitation*—published, we are proud to recall, by this Society—to realize that what they have mastered with so much effort was already well under his control in 1918. So remarkable was this achievement that I once asked him if any aspect of the idea had previously presented itself independently to him. He answered, "No" ; Einstein's theory had come as a complete novelty and had changed the direction towards which his general philosophy had been moving. It is tempting to attribute this to a general receptiveness of new ideas, but subsequent events make this hard to sustain. In most matters the groove of his thinking was cut so deep that only with difficulty, if at all, could the thoughts of others enter it. Eddington's philosophy took in the main a pre-determined course, and we must conclude that it was already prepared for the stream of relativity which was to flow along it as readily as though it had cut its own passage. Strange flowers were to grow along the banks, not yet fully to be appreciated; but of that hereafter. It must be remembered that Eddington saw every problem *sub specie aeternitatis*, and to such a mind a principle like that of relativity must have insisted on immediate acceptance or rejection. A decision could not be postponed, for on it depended the light in which every problem was thenceforward to be seen.

The Mathematical Theory of Relativity appeared in 1923. In this book, and particularly in the Introduction, we get the first, and in some respects the clearest, account of the fundamental view of physical science which determined the whole ensuing development of his ideas. It deserves the most careful study, for the manner in which the impact of relativity changed the pre-existing conception of the meaning of physics was markedly different in Eddington and in most of his contemporaries ; and herein lies, beyond doubt, the source of the difficulty which other thinkers have had in understanding his later work. Very briefly, the position may be stated thus. In pre-relativity physics an external world was contemplated, having a fixed objective character which it was the object of physics

to discover and describe. Physical measurements were the direct determination of objective features of this world, and as such had an essential independence of the observer. They might, of course, be erroneous, but there were actual correct values to which they approximated more or less closely. Relativity destroyed this view by showing that in all the measurements we commonly made there was an inescapable subjective element, which had to be separated out before one could legitimately draw any conclusions about an external world. The problem was thus posed : How shall we now regard the relation between our measurements and the external world ? I think it is correct to say that the majority view—represented, for instance, by the various schools of logical empiricism in philosophy and by Bridgman and other “operationalists” in science—is that measurements exist first of all in their own right, representing only the operations which yield them, and that our picture of the external world must take the form imposed on it by the necessity of integrating those measurements into a rationally coherent system. We start, therefore, not with an external world which we imperfectly observe, but with observations themselves, our description of the external world being our attempt to rationalize them.

Eddington took a view which lay between this and the older view which it displaced. He acknowledged the purely operational definitions of measurements and physical quantities, but posited in addition an external world having certain “conditions” which were related in some indefinable manner to the measurements. When you measured a length you did not, as in the older view, discover the magnitude of an objectively existing length in the external world ; you determined a “physical quantity” which was “defined by the series of operations and calculations of which it is the result”. This is pure operationalism, but Eddington added the postulate that the measurement represented in some way a “condition of the world” existing objectively and independently outside. Very different operations, such as measurements of length and parallel, for example, might correspond to the same condition of the world ; hence the relation between such conditions and physical quantities was not one of resemblance. We could not, in fact, say anything at all about the relation, except that it existed ; the “world” with its “conditions” was essentially mystical and unknowable ; all we could do was to deduce its “structure” never its “essential nature”, and even of that we knew only that it was expressed metaphorically by the mathematical relations found between physical quantities.

This altogether inadequate, but not, I think, false, account of Eddington’s philosophical axioms may perhaps help to explain why his later work did not meet with the understanding which he expected. The inscrutable “conditions of the world” hung like the Old Man of the Sea round the neck of his thought, contributing nothing and serving only to retard its progress and obscure results which, expressed simply and directly in terms of the essential measurements alone, might have commanded understanding and acceptance. This was particularly unfortunate because, from this point onwards his attention was given more and more to the construction of what, for want of a better term, might be called a general theory of knowledge—a systematic scheme of conceptions which, seen from one side, is theoretical physics and, from another, scientific philosophy. It is impossible to separate Eddington’s general scientific work from his philosophy, and indeed, in this respect he was well in advance of most of his contemporaries, to whom science is one thing and philosophy another, the one which they do not favour being spoken of with greater or less disrespect. It is therefore all the more regrettable that he who in many ways was better fitted than anyone else to annihilate a false antagonism was forced to express himself in a language which neither party could understand. A series of publications—*The Domain of Physical Science* (in *Science, Religion and Reality*) *The Nature of the Physical World*, *Science and the Unseen World*, *The Expanding Universe*, *New Pathways in Science*, *Relativity Theory of Protons and Electrons*, and *The Philosophy of Physical Science*—all but one written for the layman as well as the physicist, present the ideas of the theory in its various aspects.

What such a mass of literature, coming from a master of exposition about work of his own creating, has failed to make clear it would be idle to attempt to outline here. Suffice it to say that the theory was an attempt at harmonizing relativity and quantum physics by presenting the characteristics of protons and electrons as characteristics of the universe seen from a particular angle ; the smallest things in our map of the structure of the world were equivalent to the largest, in that they shadowed forth the same

"condition of the world". This was not an empty paradox. A mathematical scheme was constructed in which the radius of the universe was expressed in terms of the number and mass of the elementary particles. Some of the relations deduced are certainly impressive, and Eddington was convinced that they were deduced by pure reason, without assistance from knowledge obtained by experiment or observation. He did not, as has sometimes been asserted, claim that all knowledge, even in physics, was obtainable in this way; it was the fundamental laws and constants of nature, not the relatively accidental characteristics of particular objects, that he claimed to be able to derive from the principles of thought alone.

It is natural for those who knew Eddington only through his writings to look upon this work as the product of an illusion, and, indeed, in terms of objective likelihood, it is difficult to do otherwise. Those who knew him personally, however, will, I think, agree that the matter has another aspect. The idea of the "great man", different in kind and not merely in degree from the general run of humanity, is (no doubt rightly) out of fashion, yet it was impossible not to feel that Eddington was gifted with an exceptional insight into the fundamentals of scientific thinking, and had an intuitive apprehension of things which, when they can find expression in generally acceptable terms, will be seen to be both true and vitally important. There was an air of conviction about him which bore the stamp of genuineness. I would venture the opinion that his failure to convince others was due neither to the falsity of his ideas nor to any defect in his expression of them in terms satisfactory to himself, but to that mental peculiarity to which I have already alluded, which prevented him from understanding the way of thinking common to most of his colleagues. In matters of common agreement his complete mastery of his subject was unmistakable. Here, you felt, on reading his account of something which you already understood, is the perfect exposition; no one can fail to understand and acknowledge the inevitability of this reasoning. But when you approached a paper on his own theory, though you recognized the same master at work and found no sign of hesitation or uncertainty in the march towards the goal, you followed in blank incomprehension, soon losing all power to be surprised even if at length you came to something patently absurd.

The situation was exasperating. The conscientious thinker could not ignore what he felt to be the duty of reading the riddle, and enquiry served only to show more clearly than ever the impenetrable barrier of incompatibility between Eddington's fundamental axioms and his own. To take a single example, after struggling with what must have been one of his last and most fundamental attempts to explain his ideas—"The Evaluation of the Cosmical Number" (*Proc. Camb. Phil. Soc.* 40, pt. 1, 37, 1944)—I wrote him, not many weeks before his death, asking for light on a number of points, both general and particular. For instance, "The use of the terms 'measure', 'measurable', etc.", I wrote, "in the 'prologue' to physics inevitably suggests that the things represented thereby are later to be identified with the things so named in ordinary physics, and one cannot help thinking of them in that way. This seems to be encouraged by the example of distance on p. 38. Yet later I read: 'The basal measure . . . is the energy tensor', and 'a measurable is one kind of particle'. There is a sense in which I can agree that a measurement of distance involves four entities, but no sense at all in which I can say the same of a kind of particle". The reply to this was: "You are a bold man to set any limits to what a 'particle' may mean since the dear old classical particle became obsolete." This liberty which he assumed of tacitly changing the meaning of words with the progress of ideas is, indeed, a clue to his thought, and those who cannot think the dear old classical particle will let itself be snuffed out by an article may be helped by the realization that any of his apparently incomprehensible remarks about familiar things may be unrecognized re-definitions. But it is far from being a complete clue, and much further labour is necessary before the ordinary reader can reach the point of view from which Eddington's account of his ideas really expresses their meaning.

He himself was as puzzled as others by the situation. "I am interested in your detailed criticism", he went on, "because I am continually trying to find out why people find the procedure obscure. But I would point out that even Einstein was once considered obscure, and hundreds of people have thought it necessary to explain him. I cannot seriously believe that I ever attain the obscurity that Dirac does. But in the case of Einstein and Dirac people have thought it worth while to penetrate the obscurity. I believe they will understand me all right when they realize they have got to do so—and

when it becomes the fashion 'to explain Eddington'." From this view I would not care to dissent.

I do not think I am deceived in discerning in his later work a tendency towards a point of view which I at least might find it possible to share with him and from which his ideas might appear in intelligible form. The later part of *The Philosophy of Physical Science* (his last published book) shows for the first time a willingness to question the axiomatic basis of his philosophy, and gives some indication that he might ultimately have brought it into conformity with that of others. It is probably this development that Professor Temple had in mind when, in a passage with which I wholly disagree, he wrote (*Observatory*, 66, 9 (1945)) that Eddington's "professions of subjectivism or solipsism were semi-jocular exaggerations". They are neither properly denoted by the term "solipsism" nor, I am convinced, anything but expressions of fundamental convictions. On such matters Eddington could not be trivial. He might be profoundly wrong, but he would inevitably be profound. His playfulness found sufficient scope in his method of exposition, where, indeed, though always delightful, it was sometimes an obstacle rather than a help to understanding. It is picturesque to imagine the electron measuring up the local radius of curvature of space-time and adjusting its dimensions accordingly, but the metaphor does not bring to all minds an immediate understanding of the underlying physical relation. Nevertheless, the relation was an essential part of his philosophy, and in the matters to which Professor Temple refers, the truth towards which, as it seems to me, he was unconsciously moving was simply that since the ultimate evidence for any assertion at all one makes about the world must lie in his own experience (even if, to use ordinary language, it rests on someone else's reasoning or experience, one is able to adduce that only on the evidence of his own experience of hearing or reading of it), a systematic deduction from evidence to conclusion must necessarily begin with the experience one has one's self. In particular, the assertion of the "existence of other people" must be established on this necessary basis if risk of self-contradiction is to be avoided. Eddington had long since realized the necessity for this, but had not taken the final step of yielding to it completely. In *The Nature of the Physical World* (1928) he wrote: "The only subject presented to me for study is the content of my consciousness". In *The Philosophy of Physical Science* (1939) he returned to the subject, and felt the necessity of reconciling this view with his references to "other people", but did not get further than arbitrarily postulating that other people must be supposed to exist. Possibly his reluctance to accept the inevitable implication of his doctrine arose from the fear that an attempt to formulate the meaning of the phrase "the existence of other people" in terms of the experiences of his own which gave it legitimate significance might degenerate into, or be regarded as equivalent to, a denial that other people "exist" in the absurd sense in which that doctrine is generally denoted by the name "solipsism". I am convinced, however, that, had he lived, he would have removed this defect in his reasoning, and in 1940 I wrote (*Observatory*, 63, 25): "I venture to prophesy that, if he is granted the years an astronomer has the right to expect, he will take this step." Those years, alas! were not allowed him.

As a man Eddington had a strongly attractive personality with which, paradoxically, it was difficult to come into close relationship. Tall, well-built, handsome in youth and an imposing figure always, he would draw a second look in any company. His interests were many, and not confined to the realms of pure reason. He had a wide knowledge and keen appreciation of English literature, but could yet enjoy a well-conceived detective story without being either unaware of or unduly repelled by its literary mediocrity. He was a crossword puzzle addict, and enjoyed a game of golf, though his favourite way of spending a holiday was to mount his bicycle and disappear as completely as possible from human ken. This practice, like the most obvious of his characteristics—an extreme shyness—might easily but wrongly be taken to denote a natural shrinking from human intercourse. On the contrary, he appeared to desire fellowship with others who shared any of his numerous interests—a quality nowhere more in evidence than at the dinners of the Royal Astronomical Society Club, of which he was a member for many years and, at the time of his death, Vice-President and a "double-centurion". His reserve appears rather to have originated in the natural difficulty which he always had in bringing his thoughts into line with those of others, coupled with a slowness of expression which was perhaps not unrelated to, though not entirely a consequence of, a scrupulous care for ultimate exactness. Of the first point, the peculiarity of his outlook on fundamen-

physical problems, already alluded to, is an outstanding example ; it remains only to add that, unlike most shy people, he had little self-consciousness, but was strongly self-centred. If he reviewed a book (which he rarely did, knowing his natural unfitness for the work) he would tell the reader, of whose expectations he appeared to be quite unaware, little or nothing of the author's aims and achievements, but would deal only with the points, no matter how subsidiary, which related to his own work and interests. This was not *because* they related to his own work ; the work rather had become his own because he thought it of major importance, and he appears really to have believed that he was giving a proper delineation of the book by restricting attention to it.

His slowness of expression revealed itself most prominently in unprepared discussions and controversies. Here he would show to such poor advantage that a stranger might have been pardoned for imagining that he had not previously given any thought to the subject. He would begin a sentence, pause, start another, return to the first, the whole process being accompanied by characteristic slight and unrevealing gestures of the hands and lips, and finally sit down abruptly without even reaching the anti-climax which was well in sight, leaving the other controversialist to wonder whether the discussion was ended, and, if not, whether he could do anything more useful than repeat his previous point. When the written account of the discussion appeared, however, the chances were that Eddington's case would appear complete and final. It was the same in private conversation. Unless one knew him well, a talk was apt soon to peter out in an awkward silence which it was difficult to terminate. The point of discussion having been dealt with (not necessarily settled), his interlocutor had the feeling that a mental chasm which had momentarily been bridged had opened up again. Eddington, too mistakenly kind-hearted to walk abruptly away, and yet finding nothing to say, would lapse into his own meditations, while his companion would stand uncomfortably waiting for the occurrence of some process of physical disconnection for which no natural mechanism existed. A distinguished foreign astronomer, familiar with his writings and expecting, on meeting him for the first time, to hear a ready elucidation of his problems, said afterwards in a tone of bewilderment : "I was never more surprised. He can say 'Yes', and he can say 'No', and that is all that he can say !"

Eddington had a keen sense of humour, and a subtle though not a ready wit. Here, again, time was necessary for the manifestation of his qualities. An occasion in 1928 comes to mind on which, running out of matches for his indispensable pipe, he entered a shop in a small German town and found that the necessary word had escaped him. A period of ineffective murmuring at length culminated in the word "Lucifer !" uttered explosively at the startled and uncomprehending girl behind the counter. Only later did the master of expression get his meaning across by the act of striking on an imaginary box. Yet in retrospect he could enjoy the situation as well as another.

I have said little of Eddington's astronomical work in the relatively narrow sense, outstandingly important though it is, for that comes more fittingly within the province of another Society. To us he was a physicist in the most fundamental and comprehensive sense of the word, whose Presidency of our Society is among our most cherished traditions. Honours were showered upon him, which also will be recorded elsewhere. He received them with pleasure and gratitude and with no affectation, knowing well that they were but the guinea stamp, and conscious, without false conceit, that they were impressed on gold. This notice makes no attempt at a complete presentation of this many-sided genius. I have tried merely to indicate what seem to me to be the most significant elements of his work, and at the same time in some measure to preserve for those who knew him, and create for those who did not, a partial picture of one of the most remarkable men whom it has been my good fortune to know.

HERBERT DINGLE.

CHARLES GLOVER BARKLA, F.R.S., NOBEL LAUREATE

THE name of Barkla will always be associated with the K and L characteristic X-radiations which his brilliant series of researches revealed before the nuclear theory of atomic structure had been enunciated, and while the discriminating feature of a beam of X-rays was still its penetrating power.

Born in Widnes on 7 June 1877, Charles Glover Barkla was the son of John Martin Barkla, secretary to the Atlas Chemical Company of that town. He was educated at the Liverpool Institute and at University College, Liverpool, and graduated in 1898, obtaining first-class honours in physics. In the following year he was awarded a research scholarship by the Royal Commissioners for the Exhibition of 1851 and proceeded to Cambridge, entering Trinity College as an "advanced student" admitted to a course of research. Barkla's early work at the Cavendish Laboratory was an investigation of the velocity of electric waves along wires, a research in which he used a magnetic detector of the type designed by Rutherford. An account of this work is published in the *Philosophical Magazine* for 1901. During his third, and last, year at Cambridge, Barkla began the comprehensive series of experiments with X-radiations which brought him recognition as an experimentalist of the highest rank.

It had been observed by Röntgen, who seven years earlier had discovered X-rays, that a gas exposed to these rays became a source of secondary radiation. This radiation was the subject of Barkla's experiments. At an early stage in his investigations he discovered that the secondary rays were of two kinds: one kind, which was obtained when the primary beam traversed gases or solid elements of low atomic weight, was found to be similar in quality to the primary radiation, while the other kind, obtained most strongly when elements of high atomic weight were irradiated, was always found to be more absorbable than the primary radiation which gave rise to it. Barkla showed that the former was produced by scattering of the primary beam, the scattering centres being the electrons in the atoms of the irradiated substance. Using the theory of scattering developed by J. J. Thomson, which assumed that X-rays consisted of a succession of electromagnetic pulses, Barkla calculated the number of electrons in the atoms of the various light elements on which he experimented. His results were corroborated later by Rutherford's measurement of the nuclear charges of these atoms. Barkla investigated also the angular distribution of the scattered radiation, and obtained results which gave further support to Thomson's theory of the nature of X-radiation. This stage of his work culminated in the establishment of the fact that the secondary radiation from carbon, scattered in a direction perpendicular to that of the primary beam, was plane polarized, a result of fundamental importance in connexion with the conflicting views then held as to the nature of X-rays.

The other kind of secondary radiation—that which was more absorbable than the primary—was found to be characteristic of the irradiated substance and, moreover, could only be excited when the incident radiation had a penetrating power exceeding a certain minimum, peculiar to the substance. Its production was accompanied by a selective absorption of the primary, and, in contrast to the scattered rays, this characteristic or "fluorescent" radiation—as Barkla named it—appeared at first to be homogeneous, even when the primary beam exciting it comprised radiations of widely different powers of penetration. Barkla subsequently showed that the characteristic radiation could be resolved into two components of very different penetrating powers, and further, that on irradiating elements of successively increasing atomic weights, the resulting characteristic radiations were increasingly more penetrating. Of these two component radiations the more penetrating, or K radiation, proved so homogeneous in regard to absorbability that it was regarded as constituting a single spectrum line, whereas the less penetrating component—or L radiation—showed heterogeneity, which suggested that it consisted of more than one line.

The absence from the characteristic radiation of any evidence of polarization, its uniform distribution around the radiating substance, and the manner of its variation in intensity with variation of quality of the primary beam, all of which phenomena Barkla discovered in the course of his investigations, showed that it was produced by a process very different from that which gives rise to the scattered rays. Barkla's first attempts to explain how the characteristic radiation originated were necessarily very tentative. Experimental results indicated that a much more important part must be assigned to processes taking place within the atoms of the absorbing substance than had been necessary in accounting for the scattering. As Thomson's theory had proved so successful in interpreting the scattered radiation, an attempt to extend it to cover also the characteristic type was the most natural line of approach. Since the radiation was characteristic of the irradiated element, and was more easily absorbed than the radiation giving rise to it, it

could not originate simply in the response of a free electron to the intense electric field of the primary pulse. The fact that it was emitted most strongly by elements of high atomic weight suggested to Barkla that an explanation might be found by considering the disturbing forces exerted by neighbouring charged particles on an electron set in vibration by an incident electric pulse. Such disturbances, which would be most marked in the case of elements of high atomic weight, on account of the greater number of electrons in their atoms, might result, Barkla thought, in the emission of a pulse more complex, and hence more easily absorbed, than the primary pulse.

Barkla continued to discuss his results in terms of ether pulses until 1913, when the diffraction of X-rays by crystals demonstrated the essential similarity of X-rays and ordinary light, and confirmed the conception of X-ray wave-lengths. At about this time, ideas concerning the structure of atoms were being considerably clarified. Rutherford established the existence of a small massive positively-charged nucleus, Bohr published his theory of the arrangement of extra-nuclear electrons, and Moseley's photographs of X-ray spectra, showing the progressive shift of corresponding lines towards shorter wave-lengths as the atomic weight of the emitting element increased, indicated that the inner shells of electrons were responsible for the emission of the characteristic rays. Attempts to account for these in terms of disturbances within a Rutherford-Bohr atom were made by Thomson, Bohr, and Moseley, but Barkla propounded a more satisfactory interpretation. His views were published in 1915 and elaborated in the Bakerian lecture which he delivered to the Royal Society in the following year. His experiments had convinced him that, for each electron emitted directly from the K shell of an atom by absorption of energy from the primary beam, there was emitted also one quantum of characteristic K radiation, possibly accompanied by quanta of radiations of smaller frequencies. He had shown, further, that the emitted electron took no part in the production of the characteristic radiation, and he therefore concluded that the latter originated in some process taking place within the ionized atom as it regained the normal state. From a consideration of the energies of the characteristic and of the corpuscular radiations, together with the magnitude of the absorption of energy from the primary beam, Barkla showed that this readjustment took place in successive stages. The first process, which was accompanied by the emission of K radiation, consisted in the replacement of the emitted K electron by one from the L shell; the filling of the gap thus created in the L shell by an electron from the M shell caused the emission of a quantum of L radiation; and so the process continued through successive shells until, finally, a free electron was captured into the outermost shell of the atom. For the discovery of the characteristic radiation and this explanation of its origin Barkla received the Hughes medal of the Royal Society in 1917, and was awarded the Nobel prize for physics for the same year.

The long series of investigations which Barkla began in Cambridge was continued by him in three different universities. He left Cambridge in 1902 on his election to the Oliver Lodge fellowship of the University of Liverpool, and during the years 1905-9 he was successively demonstrator, assistant lecturer and special lecturer in the physics department of that university. In 1909 he succeeded H. A. Wilson in the Wheatstone chair of physics in the University of London (King's College), on Wilson's appointment to follow Rutherford at Montreal. Barkla held the Wheatstone professorship until 1913, when he accepted the chair of natural philosophy in the University of Edinburgh. He was able to continue his investigations without serious interruption throughout these changes of domicile because of the simplicity of the apparatus he employed, which did not require a long time for reassembling on starting work in a new laboratory.

In his Bakerian lecture Barkla gave a preliminary report of a new effect attending the passage of a beam of X-rays through certain light elements—an effect to which he gave the name "J-phenomenon", and which formed the subject of most of his investigations after the year 1917. Certain discontinuities in the absorption curves of these elements which occurred for shorter wave-lengths of the primary beam than corresponded to the production of characteristic K and L radiations were at first thought by Barkla to indicate the presence of a new series of characteristic radiations—the J series.

Investigations of the scattered radiation, however, showed that a phenomenon of a different type was involved. It appeared from Barkla's experiments that the primary and the scattered rays might be absorbed to the same extent in passing through a given substance up to a certain critical thickness of that substance, after which the scattered

radiation proved more absorbable in that substance than the primary. However, even after the stage of different absorbability of the primary and the scattered radiation in one material had been attained, the two radiations might show the same penetrating power in a different material. These effects were somewhat erratic in their reproducibility, but their frequent occurrence convinced Barkla that the processes giving rise to the J phenomenon were quite distinct from those responsible either for scattering or for the excitation of fluorescent radiation. Despite the apparently capricious occurrence of the phenomenon, Barkla was confident of its reality. He was convinced that it could not be attributed to any spurious action of the apparatus. In the belief that he was dealing with a fundamentally new effect, he spent much time in attempting to sift the evidence and in trying to elucidate the conditions necessary for obtaining the different effects reproducibly. There is, however, no published record of his having arrived at a complete understanding of the matter.

Barkla was an excellent lecturer, endowed with a powerful sonorous voice which enabled him to address large classes without physical effort. As a teacher he took much trouble to promote the interests of individual students, and was successful in inspiring his abler students with enthusiasm for research work. He was in continual demand in British universities as an examiner in physics and, as a means of supplementing his professorial stipend in the interests of his family, he devoted much time to this work over a period of several years. His varied experience of students in Liverpool, London, and Edinburgh, the wide range of his knowledge of physics, his thoroughness and conscientiousness made him an ideal examiner. He took great pains to arrive at a just decision in the assessment of border-line cases, and his powers of discrimination commanded the respect of his co-examiners.

Barkla became a Fellow of the Physical Society in 1910 and was elected to the Fellowship of the Royal Society in 1912. He served for periods as a member of the council of each of these bodies. The University of Liverpool conferred the honorary degree of LL.D. upon him in 1931.

To many of his contemporaries in Cambridge, Barkla was known chiefly for his remarkable singing voice. It was, indeed, freely predicted that he had a great future before him as a professional singer, and it was sometimes said that he was missing his real vocation in devoting his time to physics. After one year as an undergraduate at Trinity he migrated to King's in order to join King's College choir and have the joyous experience of singing in the magnificent chapel of that college. On occasions when he was due to sing the solo part in an anthem the chapel was invariably crowded. In those days the original Cavendish Laboratory had only been enlarged by the provision of a room for elementary practical classes, and accommodation for research students was limited. Barkla had to carry out his experiments in the cellar of the porter's lodge, which had windows opening into a space underneath a large grating in the footpath of Free School Lane. It was Barkla's habit on arrival in the mornings, after making preliminary adjustments to his apparatus, to burst into song while waiting for things to settle down. In summer time, when the windows of his cellar were open, passers-by, on their way to the various laboratories and museums which were approached through the gateway of the Cavendish, would stop and look around with astonishment at the volume and quality of the vocal efforts which arose apparently from the bowels of the earth !

While a lecturer at the University of Liverpool, Barkla married Mary Esther, elder daughter of the late John T. Cowell, Receiver-General of the Isle of Man, and they had three sons and a daughter. The sudden death of the youngest son, Flight-Lieutenant Michael Barkla, M.B., Ch.B., at Carthage in August 1943 was a great sorrow to the family. He had had a brilliant career both at school and at the university, and seemed destined for a very distinguished future.

In his private life Charles Barkla was a man of firm religious principles. To his wife and family he gave unstinted devotion. To his closest friends he was the embodiment of kindness, loyalty, good humour, and commonsense. It was part of his personal charm that he never lost the capacity to laugh at himself with his friends. He would, for instance, smilingly recount how, a few years ago, his students produced a physical "alphabet" containing the couplet :

"J's a phenomenon known to the Prof.
On Friday its working, on Monday its off."

Recreation for Barkla meant his home or a holiday with his family and the car, preferably in the Highlands. He was physically robust and enjoyed good health until the last year of his life, when, in June 1944, illness compelled him to undergo an operation. He seemed to have recovered his normal health again by the beginning of the present session, but suddenly he collapsed, was ill for a few days, and died on 23 October.

FRANK HORTON.

JOHN RODERICK ENNIS SMITH

JOHN RODERICK ENNIS SMITH was born on 21 April 1918 at London, Ontario. He was educated at the Summerside High School, Prince Edward Island, from 1931 to 1934, and then at Dalhousie University, Nova Scotia, from 1934 to 1938. He took his B.Sc. at that University and was elected to a Rhodes Scholarship, coming into residence at Trinity College, Oxford, in October 1938. He took the D.Phil. degree in 1941. After the outbreak of war he was engaged on research work in Oxford for the Ministry of Supply, and from 1941 to 1943 held appointments as Demonstrator, first in the University Physical Chemistry Laboratory and later in the Department of Physics. In 1944 he was appointed as Scientific Officer in the Inter-Services Research Bureau. While on holiday in the summer of that same year he met his death by drowning, on 10 August, at one of the notoriously dangerous places on the Cornish coast.

In spite of the early diversion of his scientific work to war problems, he had already shown himself a man of the highest calibre in original work. His published papers are all on physico-chemical subjects, though latterly his interests began to move in the direction of pure physics. His first piece of work was a comparison of the thermal decomposition of acetaldehyde with that of its deuterium analogue. He then made a study of the kinetics of decomposition of gaseous benzaldehyde and of various substituted benzaldehydes. From this he went on to study the inhibition by small quantities of nitric oxide and by propylene of various reactions, including the decompositions in the gaseous phase of aldehydes and ketones. These studies have been of the greatest help in elucidating the problem of the extent to which such reactions depend upon the intervention of free organic radicles, and have helped very considerably in systematizing our knowledge of the kinetics of such changes. He was generally regarded by those who knew him in the Oxford Chemistry School as a man of the finest intelligence. He had a very keen analytical mind, and was not only a skilful experimenter but a good mathematician. For so young a man, working for so short a time amidst so much distraction, he has left a remarkable contribution.

Regret which must be felt, even impersonally, at the loss of such great scientific promise is multiplied immeasurably in those who knew him well. Gentle-natured, unselfish, a good athlete, and with much personal attractiveness, he inspired and gave friendship and affection in abundant measure.

C. N. H.

MARIUS HANS ERIK TSCHERNING

MARIUS H. E. TSCHERNING was born at Oestrup, Denmark, in 1854 and died in Copenhagen on 9 September 1939.

After graduating in medicine at Copenhagen in 1882, where he had studied under E. Hanson-Grut, Tscherning undertook post-graduate study in Paris and became associated with L. Emil Javal at the Ophthalmological Laboratory at the Sorbonne. The laboratory was founded in 1876 for Javal, whose translation into French of Helmholtz's *Physiological Optics* had appeared in 1867. Tscherning became Javal's assistant in 1884 and later, when Javal was incapacitated by blindness, he was appointed Director of the laboratory. He held this position until 1910, when he returned to Copenhagen to succeed Bjerrum as Professor of Ophthalmology, retiring from this post in 1925.

Following the lead of Javal, Tscherning was a great admirer of the work of Thomas Young, and delivered the first Thomas Young oration to the Optical Society in London in 1907, the year in which he was elected to Honorary Fellowship of the Society. His textbook on *Physiological Optics*, first published in Paris in 1898, was translated into

English by Carl Weiland, of Philadelphia, in 1900, at a time when no other English text on the subject was available. Written in lucid style, free from mathematics, the book became the standard students' text for some years. This would appear to account, in large measure, for the considerable reputation that Tscherning achieved in this country.

In his earlier years Tscherning was very active in investigating many problems in physiological optics. He designed an instrument, the ophthalmophakometer, for utilizing the catoptric images of the eye in measuring the curvatures and separations of the ocular surfaces. His work on the aberrations of the eye was rather severely criticized by Gullstrand. He appears to have been the first to recognize the importance of the centre of rotation of the eye in relation to the design of spectacle lenses ; and the "Tscherning ellipse", which is the graph obtained by plotting the total power of the lens against the two forms for each power that are free from primary astigmatism, is well known.

It is probably, however, for his work on the mechanism of accommodation that Tscherning is best known. The central position of his theory, first propounded in 1895, was that the general effect of the ciliary muscle is to increase the tension upon the zonule during the act of accommodation for near objects, whereas Helmholtz maintained the opposite view that the tension on the zonule is relaxed. Tscherning also stressed the importance of Young's observation that the curvature of the lens increases over the central portion only. Although he modified his theory in various respects subsequently (1904 and 1909), he did not move from his central position concerning the increased tension on the zonule. Subsequent evidence, including the important contributions of E. F. Fincham associated with the non-uniform thickness of the elastic lens capsule, leaves practically no doubt that the Helmholtz hypothesis is correct.

Tscherning's contributions to the subject of physiological optics, appearing as they did during a period of relative scarcity of original work in the subject, have been of considerable service in stimulating further enquiry.

H. H. EMSLEY.

JOHN KEATS CATTERSON-SMITH

J. K. CATTERSON-SMITH occupied the William Siemens Chair of Electrical Engineering at King's College, London, from 1930 until his death.

After qualifying at Birmingham and obtaining practical experience at the Stafford works of Siemens Bros., he had a distinguished career as a lecturer in Electrical Machinery and Design at the University of Liverpool, at Finsbury Technical College, and at Faraday House.

In 1923 he became Professor of Electrical Engineering at the Indian Institute of Science, Bangalore, where he did much to foster Anglo-Indian goodwill and co-operation. Here, he founded, and for several years edited, the journal *Electrotechnics*.

Among the papers which Catterson-Smith wrote was an early one dealing with the electric propulsion of ships, which earned him a gold medal, and later he read a notable paper on induction motors before the I.E.E. Commutation, and the design of transformers and D.C. machines were the subjects of other early papers.

His talent as a lecturer and his unusual gift for devising mechanical models of electrical phenomena were well demonstrated when, in 1932, he delivered the Faraday Lectures, sponsored by the Institution of Electrical Engineers, under the title "Everyday Uses of Electricity".

Of late years Catterson-Smith interested himself in symmetrical components. He showed some circuits for their separation and measurement at the 1937 exhibition of the Physical Society.

The Professor's health began to deteriorate during the early part of the war, and, after much suffering, he died on 25 January of this year. He will be missed both by his numerous friends and by the generations of students whom he helped so readily.

B. C. L.

REVIEWS OF BOOKS

The Royal Society 1660-1940 : A History of its Administration under the Charters. by Sir HENRY LYONS. Pp. x + 354. (Cambridge: The University Press, 1944.) 25s.

Whether the clang of the falling weights dropped by Galileo from the leaning tower of Pisa sounded the death-knell of the Aristotelian philosophy is a point that may well be disputed ; but it is indubitably certain that the end of the sixteenth and the beginning of the seventeenth century witnessed an outburst of scientific activity which is almost unexampled in history, and with which the names of Galileo in Italy and of Gilbert in England are indissolubly joined. Francis Bacon at least "rang the bell that call'd the wits together", and his Solomon's House, if it did not form a model for the societies which were springing up on every hand, served a useful end in providing material for the discussion of the constitution of a College wherein the New or Experimental Philosophy should be practised.

The precise origins of our own Royal Society are obscure ; but it is clear that, amid the drums and tramplings of the English Civil War, there existed in London (in 1645 or thereabout) a small group of men disinterested enough to meet weekly at Gresham College or at convenient places nearby to discourse of " Philosophical enquiries, and such as related thereunto ; as Physick, Anatomy, Geometry, Astronomy, Navigation, Staticks, Magneticks, Chymicks, Mechanicks and Natural Experiments These meetings in London continued and (after the King's return in 1660) were increased with the accession of divers worthy and Honourable Persons ; and were afterwards incorporated by the name of the Royal Society, etc., and so continue to this day". (Dr. John Wallis. Written in January 1696-7.)

July 15th, 1662, is the date of the sealing of the first Charter. This is the date usually recognized as marking the Society's foundation.

The young Society had the chequered career that falls to the lot of many young Societies. Subscriptions fell into arrears ; officials resigned—sometimes in what appears to have been a temper ; the Council embarked upon unfortunate publishing ventures, and found itself with many unsold copies of Willoughby's *De Historia Piscium* left upon its hands. Thereafter, the Council minutes make not unamusing reading today, though the humour would not be so evident to contemporary members of the Council. The unlucky paid officers of the Society were offered their arrears of salary in " Books of Fishes ", and Halley, set to the task of measuring the length of a degree of longitude, was offered a payment of fifty pounds or fifty Books of Fishes. The Society was indeed fortunate, during this difficult period, in possessing a clerk of the calibre of Halley, and doubly fortunate in that it was in the main due to Halley that the *Principia* was written and published. If, in the long and distinguished history of the Society, there is one day, above all others, deserving of commemoration, it is that August day, in the Cambridge of 1684, when Halley asked of Newton what would be the path of a planet under a force varying inversely as the square of the distance, and received the reply, " An ellipse " That question and reply largely determined the course of physical science during the two centuries that followed. For it was Halley who urged Newton to the continuation of his work ; who overcame Newton's constitutional aversion to publication ; who saw the work through the press ; and who published the book at his own charges, for the printer could hardly be expected to accept payment in Books of Fishes ! Halley's claims to the gratitude of the scientific world are many ; but his share in the publication of the *Principia* is by far the greatest.

The temptation to enlarge upon the many dramatic incidents in the Society's history is difficult to resist, and it is pleasant to note that Sir Henry has not been unmindful of such incidents. In particular he tells in some detail the story of the lightning-conductor controversy. In 1772, the Council of the Society appointed a committee, of which Benjamin Franklin was a member, to report upon the best form and disposition to be

given to lightning conductors ; the committee reported in favour of pointed conductors—the form introduced by Franklin—one member (B. Wilson) dissenting and expressing an opinion in favour of blunt conductors. In 1777 the opinion of the reconstituted committee was again sought, with like results. But the war of the American Revolution had by this time broken out, and the question became a political one—advocates of blunt conductors were regarded as patriotic Britons, of pointed conductors as revolutionaries !

It is credibly reported that King George III interviewed the President of the Royal Society (Sir John Pringle) and requested the Society to reconsider its decision, and to report in favour of blunt conductors, whereupon the President remarked that laws of Nature were not alterable at the Royal pleasure. At the Anniversary Meeting of 1778 Sir John Pringle did not offer himself for re-election ; *post hoc* and possibly *propter hoc*.

There are few figures in the annals of eighteenth-century science more intriguing than that of John Hill (1716–1775), and it is surprising, and indeed rather disappointing, to find him curtly dismissed by Sir Henry as “one John Hill, a quack doctor”.

Hill was versatile and a man of immense industry. Botanist, actor, dramatist, translator and doctor (his degree was M.D. of St. Andrews), he may have been most things by turns, but he was faithful to his botanical studies. He was heartily disliked by many of his contemporaries, and there is a temptation to regard as a true picture Garrick’s cutting epigram :

“For farces and physic his equal there scarce is;
His farces are physic : his physic a farce is.”

Or the less well known

“Thou essence of dock, valerian, and sage,
At once the disgrace and the pest of this age;
The worst we can wish thee for all thy damn’d crimes,
Is to take thy own physic, and read thy own rhymes.”

Which was at once capped by

“Their wish must be in form reversed to suit the doctor’s crimes;
For if he takes his physic first, he’ll never read his rhymes.”

All this goes to support the contention that Hill was vain, provoking and quarrelsome ; but when his contributions to botany are examined, they are seen to be real and substantial. He knew his plants intimately and widely; he did useful work in plant physiology and in taxonomy ; he wrote an account of the vegetable kingdom in *twenty-six volumes folio*; a more modest effort, his *British Herbal* in one volume folio, is a mine of curious information, and it would seem hardly just to dismiss as a quack doctor a man who has been selected, with Ray, Grew, Hales, Hooker, Henslow and Marshall Ward, as one of the Makers of British Botany. His quarrel with the Royal Society was probably due to his failure to obtain the necessary signatures to his certificate of candidature ; but it resulted in the publication of his *Review of the Works of the Royal Society of London* (1751)—a work which pillories the more feeble papers appearing in the *Philosophical Transactions* to that date, and which was probably no inconsiderable factor in producing a higher standard of publication in the *Transactions*.

While dealing with the matter of minor omissions, it may not be amiss to draw attention to the career of Walter White, assistant secretary to the Society from 1861 to 1883, who receives no more than bare mention of his name. White was an earnest (and humourless) Victorian, whose character had been developed in the tradition of Samuel Smiles, and his *Journals*, published in 1898, after his death, furnish a most interesting (and, on occasion, surprising) series of thumb-nail sketches of celebrities of the nineteenth century.

But these are side-issues. An authoritative history of the Society was long overdue—Weld’s history, the immediate predecessor of the present volume, was published in 1848, and brought the story down to 1830. Sir Henry’s book is primarily an “account of the way in which the Society carried on its work” ; it is based on a close and critical study of the Council minutes, and its author regards it as a preliminary study to a complete history of the Society. This may indeed be the case ; but it would seem to be somewhat in the nature of a meiosis to rate as a preliminary study a work which gives a clear and comprehensive picture of the founding of the Society ; of its early struggle for existence ;

of the period of prosperity under Newton's long reign ; of the time when the scientific work of the Society was in danger of being swamped by the number of wealthy amateurs and dilettanti recruited to the ranks of the Society ; of the dictatorship of Sir Joseph Banks ; of one period which Sir Henry terms that of the scientific revolt (1820-1860) ; and that of the later years when, as De Morgan said, "a Fellow of the Society should be a Fellow Really Scientific". It is a great story, and a story which loses nothing in Sir Henry's sympathetic hands. There is much more in the book than a cold record of administrative detail ; as we have seen, dramatic incidents in the Society's history are not passed over, and, period by period, there are given admirable biographical sketches of Presidents and Senior Officers of the Society.

It is a sad thought that Sir Henry, who had passed the book for the press, did not live to see its publication ; but he has, all unknowing, reared an enduring monument, and his labours have earned for him the affectionate thanks of all students of the history of science.

A. F.

Handbook of Industrial Radiology, by Members of the Industrial Radiology Group of the Institute of Physics. Edited by J. A. CROWTHER. Pp. viii + 203. (London : Edward Arnold and Co., 1944.) 21s. net.

This handbook, which "had its origin in a series of lectures given before the Industrial Radiological Group of the Institute of Physics", is a timely production. Although the last twenty years have seen no revolutionary changes in x-ray apparatus and technique, progress has been steady and solid, and the often meretricious exterior of the modern set conceals a triumph of material and design. Part of the story of its development may be guessed as this book is read, but the more particular purpose of the authors has been to state the principles and describe the technique of modern industrial radiology. The result is a volume which should find its place on every radiographer's bookshelf.

The book comprises nine chapters, uneven in quality, each dealing with some particular aspect of the subject. Editing has reduced overlap to a negligible amount.

Three chapters are particularly good. In that on the physical principles underlying radiography the author has made a good choice of material and, in the space available, has succeeded, without sense of overcrowding, in including the essentials in most interesting account. The chapter on *The response of photographic materials to x-rays* is well above the usual standard of writing upon that subject. The factors involved in the production of a good negative are unusually well and logically stated. Gamma radiography is the subject of another good chapter. The author has taken full advantage of the fascinating material he has had to present. Radium (or radon) may be expected to find an increasing use in the future, particularly because of the possibility of using it in situations quite inaccessible to an x-ray tube.

An adequate description of modern x-ray equipment is given in a chapter headed *Requirements in design of industrial x-ray equipment*. Improvements could have been effected in the descriptions of high-tension circuits. The author draws attention to the short lives which tubes have when operated at constant high potential ; there seems to be a simpler reason for this than he suggests. The features (good and bad) of modern cathode design would have repaid treatment. The typical industrial set is well described and a short description is given of the megavolt sets now coming into use.

A considerable fraction of the chapter on quantitative measurements is devoted to dosage. Few subjects provide so much evidence of confused thinking. From this the author is more than usually free, though an unhappy phrase in one place might reinstate the confusion in the reader's mind.

The chapter on the radiography of heavy metals prescribes a technique which the beginner might reasonably follow, though, as he gains experience, he will in some respects depart from it with advantage. The author's paragraph on the reporting of radiographs is interesting ; one would wish it longer.

Even with the standard of reproduction of this book, radiographic flaws should be indicated by arrows. It is unfortunate that the author of the chapter on the radiography of light metals should point out how the definition of a flaw is improved by filtration when in the illustration one can only guess which is the flaw and which are blemishes

in reproduction. It is also disturbing to find that a great improvement has resulted from an increase in voltage when the author points out that the opposite has occurred. The particular features of light metals from the radiographic point of view are adequately treated.

A chapter on uncommon applications of industrial radiography contains a good deal of material of popular interest. A chapter on x-ray protection concludes the book.

The production is good, especially judged by war-time standards. Very few misprints occur. The most serious are due to alignment of quotients in exponents, causing transfer of terms from numerator to denominator. Three such cases were noticed. A. G. W.

Sound Insulation and Acoustics, by the Acoustics Committee of the Building Research Board of the Department of Scientific and Industrial Research. Pp. 80. (London: H.M. Stationery Office, 1944.) 1s.

This is one of a series of pamphlets dealing with various aspects of post-war building. In a methodical way it describes current practice in the acoustical treatment of buildings, both from the point of view of preventing unwanted sound from entering a building, or passing from one room to another, and from that of obtaining desirable conditions for speaking and making music within a room. Valuable features of the pamphlet are the tables giving concise data on the noise reduction to be expected with various types of building construction and of up-to-date values of absorption coefficients of materials.

As most of the research work on sound during the war has been along lines unconnected with buildings, the reader must not expect to find much that is new. One novel suggestion is to screen the lower floors of buildings in town from street noise by planting shrubs and trees of thick foliage along the verge of the road, though, as the Committee point out, experiments are needed to show how effective such a screen would be.

The Committee is sometimes a little too optimistic as to the economic aspects of sound insulation. They consider that, for example, the constructions they advocate for insulating blocks of flats will be inexpensive, but this term must be taken in relation to pre-war conceptions. Certainly the specially isolated rooms for music practice in the home, which they propose, can never be inexpensive in relation to the urgency of their incorporation in houses and flats. A generation that has become indifferent to radios blaring into courtyards and gardens in the summer is not going to cavil at little Mary practising her scales in the adjacent dwelling.

This pamphlet can be recommended to all who want what is in fact an up-to-date and concise text of all the essentials of "Acoustics of Buildings". At a shilling, it must make all private publishing firms who have a book on the subject on their lists gnash their teeth!

E. G. R.

RECENT REPORTS AND CATALOGUES

Supplementary List of Publications of the National Bureau of Standards, January 1 1942 to June 30 1944 (with Subject and Author Indexes), compiled by J. L. MATHUSA. (Supplement to Circular C24, November 1944.) Pp. 84. U.S. DEPARTMENT OF COMMERCE, Washington, D.C. 20 cents.

Abridged Scientific Publications from the Kodak Research Laboratories, Volume 25, 1943. Pp. 443+xii. EASTMAN KODAK COMPANY, Rochester, N.Y.

A Report to the Government of India on Scientific Research in India, by Professor A. V. HILL, M.P., Sc.D., F.R.S. Pp. 55. Reprinted in the United Kingdom for private circulation. THE ROYAL SOCIETY, Burlington House, London W. 1.



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